

ABSTRACT

Title of dissertation: **CHARACTERIZATION OF MECHANICAL PROPERTIES AND DEFECTS OF SOLID-OXIDE FUEL CELL MATERIALS**

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Solid-oxide fuel cells (SOFC) have the potential to help the energy economy transition to a more efficient generation method. A challenge in SOFCs is that the composite ceramic cell must maintain a gas-tight seal between the anode and cathode while minimizing the thickness to improve performance. This seal must withstand heating and changes in oxygen content, which affect the physical and mechanical properties of the materials. To understand these effects, it is needed to investigate the effects of environment, microstructure, and macrostructure interplay on the cell's strength, modulus, and fracture toughness.

The mechanical properties of SOFC materials are difficult to study at operating conditions. Most research to date have investigated the material properties at ambient conditions after cycling a cell or at elevated temperatures in air. As part of this work, an enclosed three point bend apparatus has been built which can be heated to the same temperature and environment as an operating SOFC, measuring their properties *in situ*.

With this technique, among others, a variety of materials and systems have been characterized, including established materials, nickel-oxide and gadolinium doped ceria, to new materials such as a strontium iron cobalt molybdenum oxide. It has been determined how the choice of pore former effects the strength up to elevated temperatures, how fracture toughness and strength can increase with temperature due to relaxation of intrinsic stresses, the most likely time for failure of an SOFC is under reduction due to uniform growth of microstructure flaws and how cell orientation does not impact mechanical properties.

This new knowledge into the changing mechanical properties of the different materials and structures tested will allow for the design and optimization of SOFC devices to maximize reliability and performance. In addition, the apparatus built to measure in-situ properties can also be applied to other temperatures and gaseous environments for different applications. This work helps bring SOFCs from a theoretical lab-based technology to a reliable means of efficient energy generation for use by society.

CHARACTERIZATION OF MECHANICAL PROPERTIES AND DEFECTS OF SOLID-OXIDE FUEL CELL MATERIALS

by

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Dedication

I dedicate this to my wife, Bethany, who has encouraged and supported me throughout the process, and to my two wonderful daughters, Lucy and Madeleine. You brighten my life in ways I cannot begin to explain.

Acknowledgments

I would like to start off by thanking my graduate advisor, Dr. Eric Wachsman, for his support during my graduate career. He allowed me the freedom to direct the details of my research and the support to help me reach my goals. He was also supportive of me when my family began to grow through marriage and children, allowing me to continue to develop my personal life while pursuing my degree.

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List of Abbreviations and Symbols

po₂ partial pressure of oxygen

csv comma separated value

GDC gadolinium doped ceria

GFC gas correction factor

LSM lanthanum strontium manganite

MFC mass flow controller

MIEC mixed ionic-electronic conductor

MS mass spectrometer

NI National Instruments

PWM pulse width modulation

SFCM SrFe_{0.2}Co_{0.4}Mo_{0.4}O_{3-δ}

SOFC solid-oxide fuel cell

TGA thermogravimetric analysis

TPB triple phase boundary

YSZ yttria-stabilized zirconia

Chapter 1: Introduction

1.1 Motivation for Solid-Oxide Fuel Cell Research

The world depends on fossil fuels for its daily energy needs. This is a fact that is going to stay with us for the foreseeable future. By 2040, it is estimated that fossil fuels will still supply 78% of total energy demand. [1] Traditionally, the annual increase in demand is met by an increase in supply of fuel. This increase is supplied by developments in mining and drilling operations, although recent advances have been found to be controversial, such as hydraulic fracturing. [2, 3] These concerns do not even account for the increased emissions caused from combustion of fossil fuels and their effect on the global environment. [4–6]

An alternative to increasing the supply and use of fossil fuels is to increase the efficiency of converting the fuel into useful work. Combustion generators convert chemical energy to thermal energy, then to mechanical energy, and finally into electrical energy. Each energy conversion step has intrinsic losses which limit efficiency. SOFCs have the ability to solve this for applications where electrical power is desired. SOFCs allow for side stepping of these losses by allowing for the direct conversion of chemical energy to electrical energy. Power generation plants have efficiencies around 30%, while a stand-alone SOFC generator can convert fuel to electricity at

45 to 65% efficiency. [7, 8] SOFCs are able to run on a variety of fuel sources, such as hydrogen, methane or even biogas. [9] This fuel flexibility and higher efficiency positions SOFCs to bridge the gap in the energy economy as it transitions from fossil fuels to renewable sources. However, many technical hurdles still remain which currently limit SOFCs' viability and must be addressed.

1.2 Solid-Oxide Fuel Cell Operation

The layout for a hydrogen-fueled SOFC is presented in Figure 1.1. Fuel is exposed to the anode side of the cell, while an oxygen rich gas (usually air) is exposed to the cathode side. Separating the two sides is the cell itself, with anode, electrolyte, and cathode. The electrolyte is only conductive to oxygen ions, not electrons. A perfect electrolyte would have no electronic conduction, allowing no leakage current from anode to cathode and forcing all electrons to travel via an alternative route. At the cathode, diatomic oxygen gas will disassociate into oxygen ions, each with a 2– charge from the addition of electrons from the cathode to the oxygen. The oxygen ions then travel though the electrolyte and react with the fuel at the anode, freeing the previously captured electrons. To maintain charge balance, electrons must travel in the opposite direction to the cathode. Because the electrolyte only allows oxygen ions to diffuse though it, the electrons travel though an external circuit performing useful work in the process. A limiting factor in this movement is the ability of oxygen to transport into, through, and out of the cell. As the rate of oxygen transport is increased, the ability for electrons to perform work also increases.

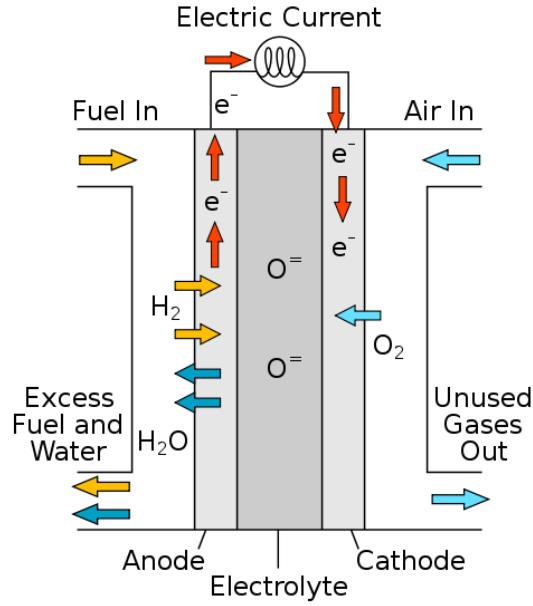


Figure 1.1: Diagram showing flow of materials in the operation of an SOFC. [10]

The driving force for the movement of oxygen ions and electrons comes from the chemical potential gradient across the cell. When the anode is exposed to fuel, it creates a low partial pressure of oxygen (p_{O_2}) in comparison to the cathode, which is exposed to air. This gradient drives the motion of oxygen through the cell from the high p_{O_2} of the cathode to the low p_{O_2} of the anode, and generates electric current in the opposite direction to maintain a charge balance. The electrical potential at open circuit conditions (voltage with no current draw) is expressed by the Nernst equation, given in Equation 1.2 for the reaction given in Equation 1.1, where f_A is the fugacity of species A, E^o is the standard potential for the reaction, and n is the number of charges involved in the reaction, R is the ideal gas constant and F is Faraday's constant. [11] Commonly, the fugacity is replaced by the partial pressure of

the species. For the case of a hydrogen-fueled SOFC, Equation 1.2 can be simplified to Equation 1.3. [12] From these equations it can be seen that the partial pressures of the involved species have a large role to play in the open circuit voltage of the cell. It is critical that the fuel and air remain separated by the cell. If there is a leak either through the cell or around it, then the electric potential across the cell will decrease harming performance.



$$E = E^o - \frac{RT}{nF} \ln \left(\frac{f_C^c f_D^d}{f_A^a f_B^b} \right) \quad (1.2)$$

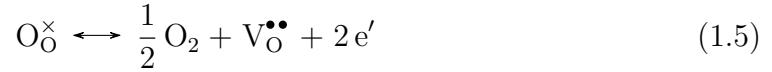
$$E = E^o + \frac{RT}{2F} \ln \left(\frac{p_{H_2}(p_{O_2})^{1/2}}{p_{H_2O}} \right) \quad (1.3)$$

While the electric potential is established by the partial pressure gradient, the electric current is limited by the ionic conduction of oxygen ions from the cathode to the anode. In ionic conduction, oxygen ions hop from site to site via oxygen vacancies, locations where an oxygen atom is missing from the site it usually occupies in the crystal lattice. Because conduction depends on vacancies, the more vacancies that are present in the lattice, the more available sites for oxygen to move between, the greater the conductance, and the greater power output of an cell. The relationship between oxygen vacancy concentration and oxygen conductance is given by Equation 1.4, where σ_i is the ionic conductivity, $[V_O^{••}]$ is the concentration of oxygen vacancies in the lattice, μ_O is the ionic mobility of the oxygen, and Z_e is the charge of the conducting species. [13] Thus, by adding more oxygen vacancies the ionic conductivity increases. While additional oxygen vacancies are a benefit to the electrical performance of the

cell, it can have detrimental effects to the mechanical properties.

$$\sigma_i = [V_O^{\bullet\bullet}] Z e \mu_O \quad (1.4)$$

During operation, oxygen vacancies are created by removal of lattice oxygen from the anode as it reacts with the fuel, as shown in the half-cell reaction of Equation 1.5. This reaction takes place on the surface of the anode, but for convenience it is written where oxygen has associated back into a diatomic state and the fuel subsequently react with it. This reaction of fuel with oxygen creates an environment with a very low p_{O_2} at the surface of the anode. A steady state concentration of oxygen vacancies will be reached as the cell comes into equilibrium with the environment, but this concentration will depend on the exact environmental, material, and performance conditions of the cell.



The cathode and anode materials must facilitate the incorporation of oxygen into the cell and the reaction with the fuel. They must also serve to transport the electrons into and out of the cell as oxygen changes state. As a result, the anode and cathode must possess both electrical and ionic conductivity. To achieve this, a mixture of the electrolyte material and an electronically conductive material are used to create these structures. This mixture of materials creates specific sites where the cell is active, known as triple phase boundarys (TPBs) and demonstrated in Figure 1.2. The TPB is the location where gas, electronic conductor, and ionic conductor meet and oxygen can incorporate into the cell or react with the fuel. To assist gas diffusion to the TPB and to maximize the length of TPBs, pores are added, greatly

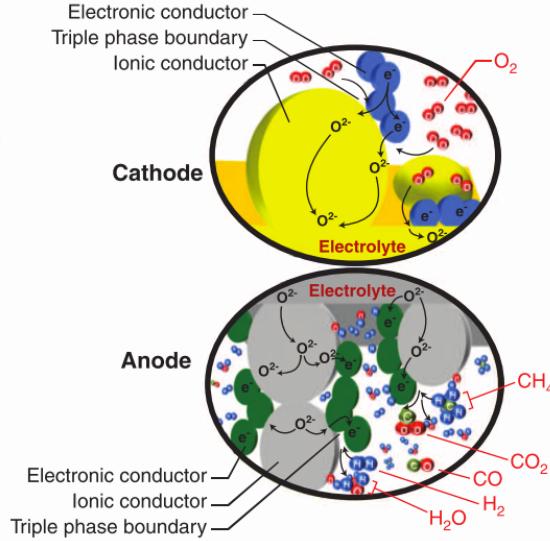


Figure 1.2: Diagram showing the triple phase boundary and the importance as being the site where incorporation and reactions occur. [7]

increasing the available surface area of the electrodes. The more TPBs that are present, the more exchange can occur between the gas and the cell at any given time and the current output of the cell is increased. This added porosity does not come without the disadvantage of decreasing the mechanical strength of the cell. [14, 15]

An operating SOFC would consist of a series of individual cells stacked together for combined power output. The cells would be sealed between current collectors and interconnects and heated to operating temperature. The elevated temperature enables oxygen conduction through the electrolyte by increasing vacancy concentration and mobility, but decreases the theoretical voltage. Historically, SOFCs operated near 1000 °C, but advances in materials now allow cells to operate at 650 °C and development continues to decrease the operating temperature. At lower operating temperatures it becomes easier to create better seals and the stack can be built from

more readily available materials. Additionally, the cells are subjected to less thermal expansion, reducing the stresses on the cell.

1.3 Solid-Oxide Fuel Cell Materials

Each structure of an SOFC is fabricated from combinations of materials designed to optimize that part's function then laminated with the other structures to create the cell. For example, a cell can be comprised of a nickel metal-gadolinium doped ceria (GDC) anode, a GDC electrolyte, and then a lanthanum strontium manganite (LSM) cathode. [16, 17] The individual parts are cast into thin flexible sheets (tapes) from bulk powders, with additives such as pore formers where appropriate, and then laminated together and co-fired to create a single cell. As a result, a completed cell has distinct layers in it where the material and properties abruptly change. This composite structure can then have inter-diffusion between layers, smoothing out the abrupt changes, but creating new structures and compositions that were not present upon lamination. [18]

The traditional material used for electrolytes in SOFCs has been yttria-stabilized zirconia (YSZ). YSZ is very stable, has a ratio of ionic conductivity to total conductivity (transference number) of approximately 1, and good conductivity at temperatures in excess of 800 °C and up to very low p_{O_2} s. A high transference number minimizes leakage current due to electronic conduction in the electrolyte, maintaining cell performance. As mentioned previously, GDC is another choice for an electrolyte. Other rare-earth doped cerias have been used as electrolytes, but

GDC tends to outperform them under a variety of conditions. At 600 °C, GDC exhibits an order of magnitude higher conductivity than YSZ, but has a smaller electrolytic domain where the transference number is near 1. [19] Under conditions of high temperature or very low p_{O_2} , GDC will start to leak electrons through the electrolyte, reducing cell performance. As SOFC operating temperatures are reduced for improved efficiency, GDC is favored for the electrolyte material.

The anode usually consists of a mixture of the electrolyte material, which provides good ionic conductivity, with an electronic conductor that can facilitate fuel oxidation reactions on the surface. In combination with an ionic conductor it creates a cermet which functions as the anode. Nickel has commonly been used in the anode due to its high conductivity and catalytic properties. A challenge with nickel is that at ambient conditions it oxidizes into nickel oxide, but at operating conditions it reduces to the desired nickel metal. There is a large lattice parameter change between nickel and nickel oxide, such that, upon reduction it decreases volume by over 15%. As a result, the overall porosity of the anode layer increases as the SOFC is put into service and the anode is exposed to reducing conditions. [20, 21]

This increased porosity can greatly decrease the flexural strength and modulus of the anode and of the overall cell. [22, 23] Additionally, nickel is prone to poisoning from sulfur contaminants in the fuel, so alternative anodes are of interest for use in SOFCs.

As an alternative, other metal-ceramic systems have been researched to serve the function of the anode. These have included copper, cobalt, and platinum systems, but each suffer from a significant drawback such as coking, long-term performance

degradation or cost. A different approach is to use an all-ceramic anode, made of a mixed ionic-electronic conductor (MIEC). Perovskite materials have easily been developed into MIECs with the use of a transition metal occupying the octahedral B-site. $\text{SrFe}_{0.2}\text{Co}_{0.4}\text{Mo}_{0.4}\text{O}_{3-\delta}$ (SFCM) is a recently developed double perovskite MIEC with multiple dopants on the B-site with a high conductivity of 30 S/cm. [24–26] Due to the all-ceramic nature of these anodes, their thermal expansion coefficients better match that of the other ceramic components of the cell, reducing sintering stresses and improving redox cycling durability. Conversely, all-ceramic anodes tend to have lower conductivity and catalytic performance.

This work focuses on the structures in the cell which give mechanical support, the anode and electrolyte. Specifically, Ni-GDC and SFCM-GDC anodes with GDC electrolytes will be investigated.. While YSZ systems have been studied extensively, the mechanical properties of GDC systems have not been throughly explored. As SOFCs are developed which operate at lower temperatures, GDC is the preferred choice for an electrolyte material due to its high conductivity. Ni-GDC serves as a reliable starting place to characterize the mechanical properties of the anode, focusing on the changes which occur during reduction as NiO reduces to Ni metal. SFCM being a new material has no available data on the mechanical properties, let alone the non-stoichiometry which occurs in the material under reducing conditions.

Various cathode materials exist which assist in the incorporation of oxygen into the lattice. The cathode must have many similar properties to that of the anode, but be stable in oxidizing environments instead of reducing. As a result, perovskite structures again are found in many of the materials. LSM is one of the most

commonly used materials, but others include doped SrCoO_3 , $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$, $\text{Ba}_x\text{Sr}_{1-x}\text{Ti}_{1-y}\text{Fe}_y\text{O}_{3-y/2+\delta}$. [27–30] The cathode does not tend to play a structural role in the fabrication of a cell, and thus is not investigated or developed in this work.

Outside the of the cell itself, several materials are needed to create a functioning stack. Metal interconnects support individual cells, holding them together, creating connections for the current to flow though current collectors and gas to flow though channels to the the cell. In intermediate and high temperature stacks, expensive metal alloys such as Inconel must be used to survive the extreme heat. As temperatures are lowered to below 600 °C more common metals can be used for interconnects, such as steel. Sealing materials are another critical component to assembly of an SOFC stack. Glasses with transition temperatures near the operating range are used at high temperatures as they can soften and flow into place creating gas tight seals. At lower temperatures new options are available, such as YSZ, vermiculite or mica gaskets.

1.4 Mechanical Properties

Ideally, an SOFC is as thin as possible to minimize diffusion path lengths and ionic resistances in the cell. [31] Realistically, the cell must be able to withstand the stresses of being manufactured, sealed, heating, and use. This means that a compromise must be made as to how the cell is supported and which components do the supporting. Traditionally, electrolyte supported cells were used with YSZ electrolytes where the thick dense electrolyte provides the structural support for the

cell. Recently anode supported cells made from GDC have been able to provide lower resistances due to the thinner electrolyte while adequately supporting the cell with a thicker anode which fuel can diffuse further into. [32, 33] Now the anode layer with its porosity, must support the majority of the stresses the cell is subjected to.

Ceramic materials used in SOFCs mechanically fail when stresses concentrate at a pre-existing microstructural flaw, overcoming the strength of the material, propagating a crack though the cell. Stresses can be intrinsic to the cell, left from lamination, sinter or cooling, or they can be applied externally during the sealing or operation of the cell. Microstructural flaws could be intentional with the added porosity or unintended flaws such as inclusions, contamination or grain agglomeration. These microstructural flaws are locations where stresses are concentrated and lead to the ultimate failure of the material.

Stresses are concentrated most by large, sharp featured flaws. As a result, in a uniform stress field, the largest flaw will usually cause failure. Ceramic materials will tend to fail where the sample is under tensile load and at a location near the point of maximum applied stress. Samples, even if processed together from the same raw materials, will each have a random sampling of flaws from the total batch, and a particular one which causes failure. No matter the care and attention paid to processing, some distribution of flaws will exist. The analysis of the distribution of flaws from a batch of samples is known as Weibull analysis and is explained in detail in Appendix A.2. To perform Weibull analysis a large number of samples must be tested, but as a result the overall size/shape distribution of flaws can be obtained. This allows for the observation of the flaw distribution and if it changes at different

points or if another phenomenon is occurring.

Most of the materials used in SOFCs have crystal structures which promote the generation of oxygen vacancies. As oxygen vacancies are produced, the inter-atomic bonding of the structure changes, which can decrease the elastic modulus and fracture toughness of the crystal. [34, 35] If the strength of the atomic bonds weakens on average, due to added vacancies, it then follows that the elastic modulus and fracture toughness of the crystal would also decrease. This relationship has been shown to fit for single grains of GDC using nanoindentation, but this does not necessarily hold true for an actual cell. [36] Grain boundaries can play a large role in the mechanical properties of a bulk sample as they can impede or enhance the propagation of a crack. For this reason microstructure combined with environmental conditions can play a large role on the overall mechanical properties of a fuel cell.

The first external stress applied to the cell, and the one most likely to result in failure, is the sealing of an individual cell into a stack, creating a gas tight seal between the anode and cathode sides. In this process, multiple cells are sandwiched with gasket seals and interconnects between them and compressed until a gas tight seal is achieved. While it is a compressive force that is applied, the cells are never perfectly flat, resulting in a flexural stresses as the cell is pressed flat. Figure 1.3 highlights this fact by using an optical profilometer to measure the flatness of a 10 cm by 10 cm Ni-GDC/GDC half-cell. It can be seen that the cell curves by over a millimeter, mostly at edges, where the seal would be taking place. It is for this reason that the study of the failure of SOFC materials utilizes flexural testing.

To help develop SOFCs into a viable technology which can stretch the gap in

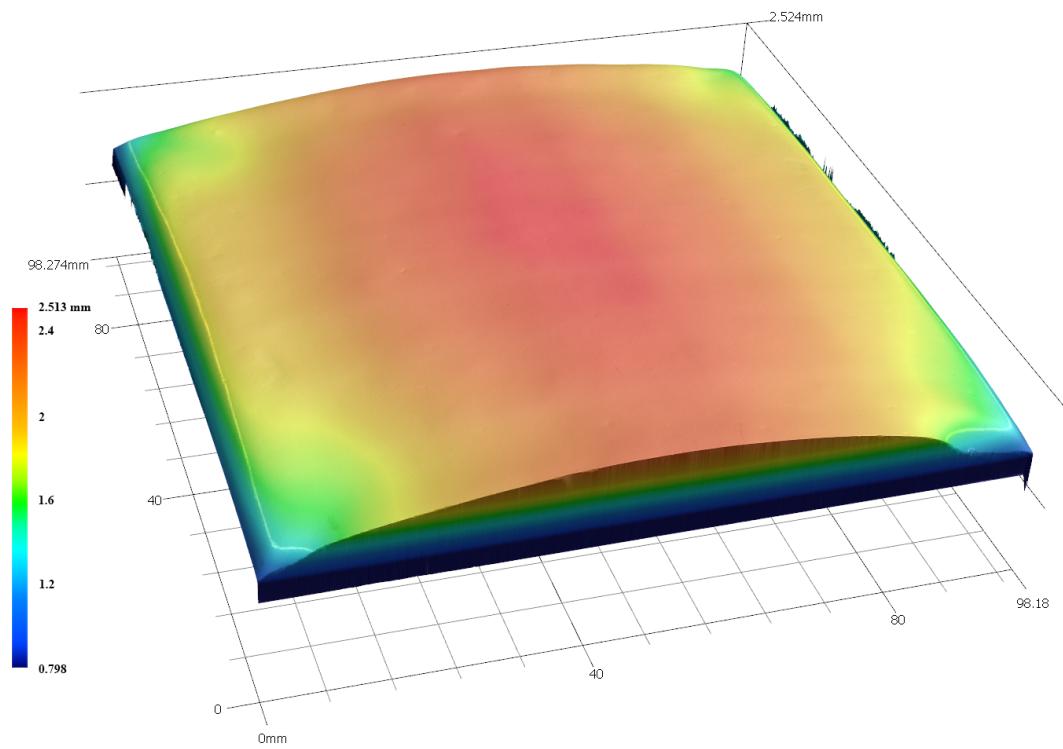


Figure 1.3: Optical profilometer measurements of a 10 cm by 10 cm Ni-GDC/GDC half-cell where the z-axis has been magnified 6X to highlight curvature

the energy economy, research is needed to improve the reliability of the cells during manufacturing and operation. This work aims to develop the understanding of fracture mechanics of real-world structures, by understanding how temperature and partial pressure of oxygen affect the strength, fracture toughness, and flaw distributions of SOFC components. This is done by analyzing the flexural properties of bulk bars and half-cell coupons at ambient conditions and at conditions similar to those found in an SOFC. Microscopy was used to look for changes in microstructure after various treatments in addition to Weibull analysis. Additionally, thermogravimetry, conductivity, and temperature programed desorption were used to understand the atomic defect structure of a new material to relate it to the mechanical properties.

Chapter 2: Experimental Procedures

2.1 Sample Preparation

2.1.1 $\text{SrFe}_{0.2}\text{Co}_{0.4}\text{Mo}_{0.4}\text{O}_{3-\delta}$ Powder

$\text{SrFe}_{0.2}\text{Co}_{0.4}\text{Mo}_{0.4}\text{O}_{3-\delta}$ (SFCM) was created from stoichiometric amounts of strontium carbonate (SrCO_3 , Sigma-Aldrich), iron oxide (Fe_2O_3 , Sigma-Aldrich), cobalt oxide (Co_2O_3 , Inframat Advanced Materials), and molybdenum oxide (MoO_3 , Alfa-Aesar) using conventional solid-state methods. The constituents were ball milled for 24 hours in ethanol and dried using a 100 °C oven. Afterwards the powder was calcined at 1100 °C for four hours.

2.1.2 Bars

GDC bars of varying porosity were fabricated using uniaxial pressing in a rectangular die. GDC10 ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$) powder was mixed with the desired volume of poly(methyl methacrylate) (PMMA) microspheres (5 μm diameter) or graphite flake to create the green body, with 0.1wt% of polyvinyl butyral added to aid in pressing and a drop of fish oil to act as a dispersant during milling. The two different pore formers were used to create differing pore geometry. The PMMA or graphite

was removed by a 400 °C pre-sintering step, and the remaining ceramic structure was sintered at 1500 °C for 4 hours. Archimedes density measurements were used to confirm porosity percent. Samples were polished with 600 grit sandpaper on all sides before testing.

Dense SFCM bars were used to maximize the total mass and mass changes during thermogravimetric testing. Samples were made by combining SFCM powder with 0.6 wt% polyethylene glycol 600, 1.8 wt% ethylene glycol, and 0.6 wt% glycerol in isopropyl alcohol and ball milling overnight. After drying at 100 °C, the powder was ground by mortar and pestle, then pressed uniaxially into rectangular bars at 30 MPa, then isostatically pressed at 30 MPa. Bars were sintered by heating to 400 °C for one hour and then 1340 °C for four hours, using a 3 °C min⁻¹ heating and cooling rate. This produced bars with 97% theoretical density by Archimedes' technique.

To create fracture toughness test samples, SFCM powder was ball milled overnight with a mixture of 0.6 wt% polyethylene glycol 600, 1.8 wt% ethylene glycol, and 0.6 wt% glycerol in isopropyl alcohol. It was then dried at 100 °C, ground by mortar and pestle, pressed uniaxially into rectangular bars at 30 MPa, then isostatically pressed at 30 MPa. Sintering followed by heating to 1340 °C for four hours at 3 °C/min with a one hour hold at 400 °C to allow the binders to burn out. This process achieved dense samples at 97% average theoretical density with no apparent flaws in the bars. Bars were then cut and sanded to final dimensions of 3 mm x 4 mm x 25 mm. The chevron notch was cut using the jig described by Jenkins, Chang and Okura following the ASTM procedure. [37, 38]

2.1.3 Test Coupons

The ASL and half-cell coupons used in the flexural testing were made using tape casting. NiO and GDC powders in a 6:4 weight ratio were mixed with ethanol, toluene, and fish oil. The mixture was ball milled on a rotary mill for 24 hours. Polyvinyl butyral and benzyl butyl phthalate were added, followed by another 24 hours milling. The resulting slurry was degassed and tape cast using a 700 micron blade height. The tapes were left to dry overnight before being cut into 12 cm by 12 cm squares. Three squares were stacked and hot pressed at 49 °C and 2 tons for 30 minutes. Following this lamination, the tape was cut into rectangular coupons measuring 25mm by 10mm. The coupons were fired at 1400 °C for 4 hours. Final bar dimensions were 8.16 by 24.15 by 2.98 mm on average. For half-cell coupons GDC electrolyte slurry was prepared and tape cast with a 40 micron blade height. After the lamination of the three ASL layers, a single layer of electrolyte tape was laminated to the ASL using the same pressure for 2 hours. The sintering procedure for half-cell coupons was identical to the ASL coupons. Samples were polished with 600 grit sandpaper on edges before testing.

Tape casting was used to create test coupons of porous SFCM-GDC ASL and SFCM-GDC/GDC half-cells. Using ethanol as a solvent, SFCM-GDC was ball milled with polyvinyl butyral, benzyl butyl phthalate, 12 µm poly(methyl methacrylate) (16 wt% with respect to SFCM-GDC), and Menhaden fish oil. The tape was cast to a thickness of 110 µm on Mylar then laminated using a hot press to a final thickness of 660 µm. Dense GDC was casted to 30 µm and laminated to the top of

the SFCM-GDC to create half-cells. Individual coupons were cut from the green tape, sintered at 1200 °C for four hours, with holds at low temperatures to burn out organic binder and pore former. The final thicknesses were measured to be 400 μm for the SFCM-GDC ASL and \sim 20 μm thick GDC electrolyte. Test coupons had their edges sanded to remove defects left from cutting, following ASTM standards. [39] Top and bottom surfaces were not sanded to preserve possible defects left from tape casting procedure, which would be representative of industrially manufactured SOFCs.

2.2 X-Ray Diffraction

X-ray diffraction (XRD) was used confirm phase purity of the SFCM after synthesis and during the testing process. A Bruker D8 Advance with LynxEye was used with a Cu K α source. A step size of 0.02° was used with a dwell of 0.8 s was used. Rietveld refinement was performed on samples as synthesized, after oxidation in pure O₂ and after reduction in pure H₂ at 600 °C for both. GSAS-II was used to perform the refinement calculations and VESTA was used to visualize the unit cell. [40, 41]

2.3 Density Measurements

Density of test bars was determined using the Archimedes method following Equation 2.1, where ρ is the density of the sample, ρ_{liq} is the density of the liquid used, w_{dry} is the weight of the sample before submersion and w_{sub} is the apparent

weight after submersion. Isopropyl alcohol was used as the liquid for measurements and samples were placed in a vacuum chamber while submerged to ensure all open porosity was filled before measuring the submerged weight.

$$\rho = \frac{w_{dry}}{w_{dry} - w_{sub}} \rho_{liq} \quad (2.1)$$

2.4 Thermogravimetric Analysis

Mass of samples during oxidation and reduction cycling was measured using a Cahn D200 microbalance. The samples were placed in a crucible suspended from a platinum wire attached to the microbalance and enclosed by an alumina tube inside a furnace. Heating control was achieved with a PID loop and temperature measurement done by a K-type thermocouple placed immediately below the sample inside the alumina tube. Gas flow was controlled at a constant 50 sccm by mass flow controllers. 21% O₂ in dry N₂ was used for the oxidizing condition while 3% H₂ in N₂ humidified with 3% H₂O was used for the reducing conditions.

To understand the degree of reduction in test coupons, thermogravimetric analysis (TGA) was used to measure the mass loss as a function of time, temperature, and gas environment. A Cahn D200 microbalance was used to measure the weight changes as the sample was heated in a furnace with controlled atmosphere. A small section of test coupon was placed in a crucible suspended from the balance and heated to 650 °C at 10 °C min⁻¹, the environment was switched from 50 sccm of 21% O₂ in N₂ to 50 sccm of 3% H₂, 3% H₂O in N₂. Mass, temperature, and p_{O₂} measurements were taken at 30 second intervals. p_{O₂} measurements were taken using

a calibrated YSZ sensor placed immediately before the sample. Samples were cooled at $10\text{ }^{\circ}\text{C min}^{-1}$ in the desired atmosphere.

Changes in mass of SFCM were measured by a Cahn D200 microbalance with the sample suspended down a quartz tube into a furnace. The furnace used to heat the sample and quartz tube was controlled by a PID controller with a K-type thermocouple placed immediately below the sample inside the quartz tube. Gas flow was controlled at consistent 50 sccm by mass flow controllers, which mixed dry nitrogen, oxygen, hydrogen, and humidified nitrogen to obtain the p_{O_2} desired. Measurements of the p_{O_2} were taken by a calibrated YSZ oxygen sensor at $800\text{ }^{\circ}\text{C}$ located before the sample. Again, intermediate p_{O_2} ranges were not able to be tested due to SFCM's incompatibility with the species required to create that environment.

Further details of the operation of the TGA and its various components are given in Appendix [B](#).

To prepare the sample, it was pre-weighed, wrapped in platinum wire and suspended from the balance, placed in the furnace with simulated air (21% O_2 , 79% N_2) flowing. Once the mass had stabilized, the furnace was heated to $800\text{ }^{\circ}\text{C}$ to allow for any organic contamination to burn off. After the mass stabilized at this elevated temperature the sample was introduced to various environments. The mass of the sample would be noted only after steady state had been reached for a condition. After testing a sample, a bar of alumina was cut to the same dimensions as the sample and the process was repeated to obtain a blank which could be subtracted from the measurements to remove buoyancy effects.

Oxygen non-stoichiometry was calculated using Equation [2.2](#), where $\Delta\delta$ is

the change in oxygen stoichiometry, MW_{SFCM} is the molecular weight of SFCM ($208.74 \text{ g mol}^{-1}$), MW_O is the molecular weight of oxygen (16.0 g mol^{-1}), w_{sample} is the weight of the sample, and Δw is the weight change as recorded by the TGA. The oxygen vacancy concentration ($[\text{V}_\text{O}^{\bullet\bullet}]$) is calculated using Equation 2.3, where ρ is the density of SFCM and N_A is Avogadro's number. To calculate the oxygen vacancy concentration, the non-stoichiometry of SFCM at a point needs to be established. For this work, based on the plateau present in the data at oxidizing conditions, it is assumed that in a pure oxygen environment ($\log(p_{\text{O}_2}) = 0$) all oxygen vacancies are filled with no oxygen interstitial or surface species, thus $\delta = 0$.

$$\Delta\delta = \frac{MW_{SFCM}}{MW_O w_{sample}} \Delta w \quad (2.2)$$

$$[\text{V}_\text{O}^{\bullet\bullet}] = \frac{\delta\rho N_A}{MW_{SFCM}} \quad (2.3)$$

2.4.1 Temperature Programmed Desorption

The effluent from the TGA was used as the inlet to a mass spectrometer (MS) to perform temperature programmed desorption. The sample was prepared as before and heat treated to remove any carbon contaminants but was allowed to cool under simulated air. It was then heated to 800°C at 5°C min^{-1} under a 50 sccm flow of nitrogen as the MS measured the 32 m/z signal which corresponded to O_2 desorption. Additional m/z signals were monitored to observed for other species.

2.5 Conductivity

Electric conductivity across p_{O_2} was measured using the four-wire technique and a Stanford SR 830 lock-in amplifier. A bar shape sample was used with dimensions of $6.46\text{ mm} \times 3.3\text{ mm} \times 1.3\text{ mm}$. Gold paste was used as a current collector, and the current range was between 0.005 to 0.05 A. A yttria-stabilized zirconia (YSZ) oxygen sensor operating at $800\text{ }^\circ\text{C}$ was used to monitor the changes in oxygen partial pressures. Intermediate p_{O_2} ranges were not tested due to an incompatibility between SFCM and the CO and CO_2 required to obtain those p_{O_2} .

Conductivity during redox cycling was measured using rectangular bars of SFCM and SFCM-GDC (2:1) composite. The samples were connected to a Keithley 2400 source meter by silver paste and wire. Using an in-house built reactor, the sample could be heated and the gas environment could be controlled. An initial measurement was taken after heating and 50 hours of exposure to 10% H_2 in N_2 , then the sample exposed cycled between air and reducing conditions over a period of 14 days.

2.6 Mechanical Testing

Measurements of mechanical properties were collected using a Tinius Olsen 10ST Universal Testing Machine (UTM) equipped with a 250 N load cell. Experiments where any samples would be tested at elevated temperatures or under reducing environments were conducted using a custom built three point flexural test fixture

placed inside a gas-tight chamber and furnace. Otherwise, a fully-articulating four point flexural test fixture was used. Samples tested at ambient conditions were placed on the appropriate testing fixture and loaded until failure. For samples tested at elevated temperatures the sample was heated in the test chamber at $10\text{ }^{\circ}\text{C min}^{-1}$, allowed to equilibrate for 20 minutes, then tested. Samples to be reduced were placed in the chamber, heated and exposed to reducing gas for 18 hours before being tested.

All tests conducted in the UTM (Tinius Olsen 10ST with 250 N load cell) were done at a rate of 0.2 mm min^{-1} with a 20 mm lower span. After measuring the force at fracture, stress was calculated using Equation 2.4 for 3-point flexural of rectangular samples, where σ_f is the stress at failure, F is the load at failure, L is the span of the fixture, b is the width of the sample and d is the thickness of the sample. At room temperature, the coupons or bars were loaded into the fixture and tested in batches of 5 per condition. Occasionally samples would break or be damaged before testing, reducing the sample set. For sample sets at elevated temperatures in ambient atmosphere, the samples were loaded into the front of the chamber, acting as a staging area, prior to heating the on fixture in the center. Upon transferring the next coupon from the staging area to the fixture, a 20 minute waiting period was used to ensure that the coupon had reached thermal equilibrium prior to testing.

$$\sigma_f = \frac{3FL}{2bd^2} \quad (2.4)$$

Following the completion of the set, all coupon pieces were cooled at a rate of $10\text{ }^{\circ}\text{C/min}$. For testing in reducing atmosphere, each coupon was reduced and tested individually. Half-cell coupons were tested in two orientations, “electrolyte-up” and

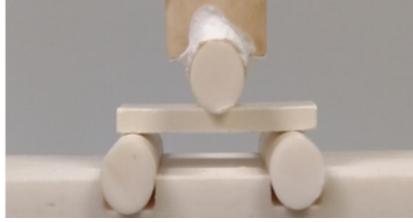


Figure 2.1: Assembled Alumina 3-Point Bend Fixture

“electrolyte-down.” These orientations cause the dense electrolyte layer to experience compressive or tensile stress. The “electrolyte-up” orientation subjects the electrolyte to compressive stress and vice-versa.

2.6.1 Development of Mechanical Test Apparatus

To develop a testing apparatus capable of simulating the various conditions experienced by operating SOFCs, appropriate materials were chosen based on thermal and chemical stability criteria. Alumina was chosen to build the bend fixture due to its chemical stability and high hardness. The sample rests crossways on two stationary 6.35 mm diameter rods which are placed in troughs separated by 20 mm. The upper half of the fixture consists of a 6.35 mm rod used to apply stress to the sample from the UTM crosshead. Both pieces are attached using silica-based cement to 300 mm rods attached at the anchor points of the UTM. Assembly and alignment is assisted with the use of a 3D printed jig to ensure repeatability. The complete alumina, 3-point bend fixture is seen in Figure 2.1 with the two bottom rollers, a sample, and the top roller making contact, applying flexural stresses to the sample.

To create the atmosphere control system, a combination of standard and custom vacuum system parts were used to enclose the bend fixture. For the main body

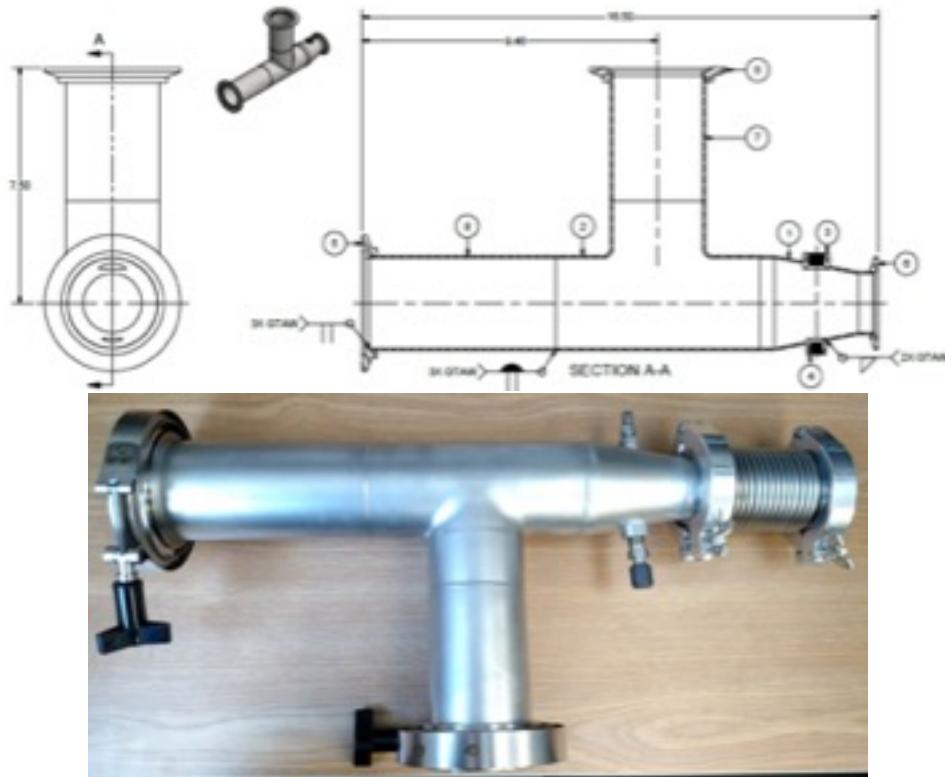


Figure 2.2: Design drawing and photo of mechanical testing atmospheric chamber

of the chamber, a 3-inch inner diameter, stainless steel tee was made with QF80 and QF50 flanges. Welded NPT ports on top and bottom allow for gas inlet and outlet and the introduction of a thermocouple through a Swagelok Ultra-Torr fitting. Figure 2.2 shows the engineering drawings and photo of the custom pieces from A&N Corp. Flexible bellows allow for the motion of the cross-bar to be translated into the fixture, requiring the subtraction of the spring force to be removed during analysis. The alumina fixture was then inserted through each end and the chamber incorporated into the furnace with QF50 to 1/2 inch tube adapters that fit over the alumina rods.

To heat the fixture and chamber, a 1 ft. cube was assembled from steel plates with cutouts on top, bottom and front. Steel wire mesh was used to create a framework inside to hold nickel-chromium alloy heating elements. Silica-based wool insulation was packed between the center cavity and the case walls. A K-type thermocouple was inserted into the chamber and used with an external PID controller to cycle the heating elements. The furnace was placed on a supporting scaffold to hold it in position during tests. The test fixture, atmosphere chamber, and furnace were affixed together as one unit and inserted into the UTM. The design was compared and qualified to a regular steel 3-point bend apparatus to ensure accurate results at room temperature.

2.6.2 Atmospheric Treatment

To test individual coupons under reducing environments, samples were loaded into the test chamber at 400 °C, after previous pre-heating in the staging area. After 20 minutes, the temperature would be increased to the desired set-point of 650 °C at a ramp rate of $10\text{ }^{\circ}\text{C min}^{-1}$ and the gas would be switched first to N₂ to flush the chamber, then to humidified argon containing 3% H₂. It would then be allowed to sit for 18 hours before testing to allow reduction. After testing, the chamber would be flushed again with N₂ and cooled to 400 °C before opening to change samples and repeat the process.

If samples had been previously reduced as a batch by exposure to hydrogen in a tube furnace and cooled under hydrogen, the atmospheric treatment was shortened,

as supported by TGA results. Pre-reduced samples were loaded into the chamber at or below 400 °C, the chamber flushed N₂, then with H₂ in Ar. After this the chamber would be heated to 650 °C, the sample tested after a 30 minute period, and cooled back down to 400 °C. At this point, the chamber would be flushed with N₂. While the chamber maintained a positive pressure of N₂, it could be opened, a new sample loaded, closed, and allowed to flush. This procedure allows for the batch reduction of many test coupons and replaced the 18 hour reduction time with a shorter 30 minute period.

2.6.3 Fracture Strength

A loading rate of 0.2 mm/min was used for all strength measurements. Strength was calculated from the maximum force measured before failure according to Equation 2.5 or 2.4 depending on if the four point or three point fixture is used respectively, where σ is the strength, P is the maximum force, L is the span width of the test fixture, b is the width of the sample and d is the thickness of the sample. Equation 2.5 is for a fixture where the top span is 1/2 the width of the bottom span. [39]

$$\sigma = \frac{3PL}{4bd^2} \quad (2.5)$$

2.6.4 Fracture Toughness

The fracture toughness of chevron notched samples were measured using a loading rate of 0.001 mm/min. Fracture toughness was calculated from the maximum force using Equation 2.6 or 2.7 for four point or three point fixtures. [38, 42] Y_{min}^* is

the shape factor as calculated by Equation 2.8, S_o and S_i are the outer and inner spans, B is the width of the sample, W is the height of the sample, a_0 is the distance from the tip of the chevron notch to the bottom of the sample, and a_1 is the average distance from the side of the chevron notch to the bottom of the sample. Each sample was measured after failure, but in this study the approximate values were $S_o = 40mm$, $S_i = 20mm$, $B = 3.0mm$, $W = 4.0mm$, $a_0 = 0.80mm$, $a_1 = 3.8mm$. Fracture toughness was measured only under air at room temperature and up to 600 °C. Under reduction the fracture toughness bars of SFCM would spontaneously fracture, preventing measurements under that condition.

$$K_{Ivb} = Y_{min}^* \left[\frac{P[S_o - S_i]}{BW^{3/2}} \right] 10^{-6} \quad (2.6)$$

$$K_{Ivb} = Y_{min}^* \left[\frac{P}{BW^{1/2}} \right] 10^{-6} \quad (2.7)$$

$$Y_{min}^* = \frac{0.38742 - 3.0919(a_0/W) + 4.2017(a_1/W) - 2.3127(a_1/W)^2 + 0.6379(a_1/W)^3}{1.0000 - 2.9686(a_0/W) + 3.5056(a_0/W)^2 - 2.1374(a_0/W)^3 + 0.0130(a_1/W)} \quad (2.8)$$

2.7 Scanning Electron Microscopy (SEM)

After fracture, SEM images were taken of the fracture surfaces. This was to observe the nature of the crack as it propagated, determining if it was transgranular or intergranular fracture, to find any flaws on the fracture which would lead to failure, and to observe pore geometry. Images were captured on an Hitachi SU-70 Schottky field emission SEM. Fracture surface images were mounted vertically and GDC samples were sputter coated with gold. Observations of porosity were taken using epoxy infiltrated samples and polished using down to a 0.25 µm diamond solution.

Chapter 3: High Temperature Mechanical Behavior of Porous Ceria and Ceria-Based SOFCs

3.1 Introduction

For planar SOFCs, a standard stack design consists of a number of square cells separated by metal interconnects. [43] These interconnects act as current collectors, gas channels, and separators to prevent fuel and air from mixing. Sealing of these stacks is accomplished by compressing the layered structure which includes sealing material. As more compressive force is applied to the stack, the quality of the seals improves. However, any cell which is not perfectly flat will experience flexural stress as a result and this can lead to cells fracturing. Due to the brittle nature of the ceramic materials that constitute SOFCs, a very thorough understanding of the mechanical limits of these devices is critical to their successful deployment.

The vulnerability of SOFCs to mechanical failure is a well-known issue. However, much of the research into this phenomenon has focused on yttrium stabilized zirconia (YSZ) based devices. [21,44,45] This material has been the standard for the field and has desirable mechanical properties but requires high temperatures to function well. As efforts are made to lower SOFC operating temperatures, a shift to ceria-based

electrolytes has occurred. Less attention has been given to the mechanical behavior of doped ceria materials across SOFC operating conditions.

Much of the study of fracture in ceramic materials has been done on technical ceramics for medical applications and for coating metal components. [46–53] These materials are optimized for fracture toughness and durability and very rarely experience temperatures above a few hundred degrees Celsius. The fracture surface analysis and correlations between microstructure and strength described for these materials are a valuable starting point for investigating fuel cell materials. However, there is a lack of extensive investigation into the properties of IT-SOFC materials at their expected operating temperatures and environments.

Efforts have been made to comprehensively examine the mechanical properties of SOFC materials and the effect of non-standard conditions on those properties. Nakajo et al. conducted a wide ranging study of materials used in anode supported SOFCs which included some attention to temperature and atmosphere effects. [45] While providing a solid base of material knowledge, this work did not fully cover materials beyond YSZ and there remains a need for further testing, especially for doped ceria. Flexural strength and Young's modulus measurements for gadolinium doped ceria (GDC) have been carried out in ambient conditions by Yasuda et al. [54] They characterized the effects of sintering temperature on density and the resulting mechanical properties. Further testing of this material system at elevated temperatures and anode gas reducing environments must be done to fully understand the mechanical behavior of GDC.

This study presents the results of a broad range of flexural tests involving the

materials used in ceria-based anode supported SOFCs along with the assembled half-cells. Using a purpose-built temperature controlled environmental chamber installed in a universal testing machine (UTM), porous doped ceria bars, anode support layers (ASL) composed of nickel and doped ceria cermet, and half-cells composed of an ASL and a doped ceria electrolyte were tested. The various test conditions used included expected operating temperatures (450 °C–650 °C), and both reducing and oxygenated atmospheres. These variations in test conditions are important because these cells must maintain their integrity from when they are first placed in a sealed stack to when they reach operating conditions. In particular, this study was intended to determine at what point in their life SOFCs are most vulnerable to mechanical failure and the mechanisms involved. Additionally, the effect of the anode-electrolyte interface on flexural strength was explored.

3.2 Results

3.2.1 Porosity and Pore Former Choice

As expected, GDC bars with greater porosity displayed lower flexural strength values as compared to less porous samples. The relationship between porosity and strength followed an exponential trend. This behavior is well established for porous ceramics and is described by Equation 3.1, where σ_f is the flexural strength with porosity, σ_o is the flexural strength without porosity, η is a geometric constant dependent on the system, and P is the volume percent porosity of the sample. [55]

$$\sigma_f = \sigma_o e^{-\eta P} \quad (3.1)$$

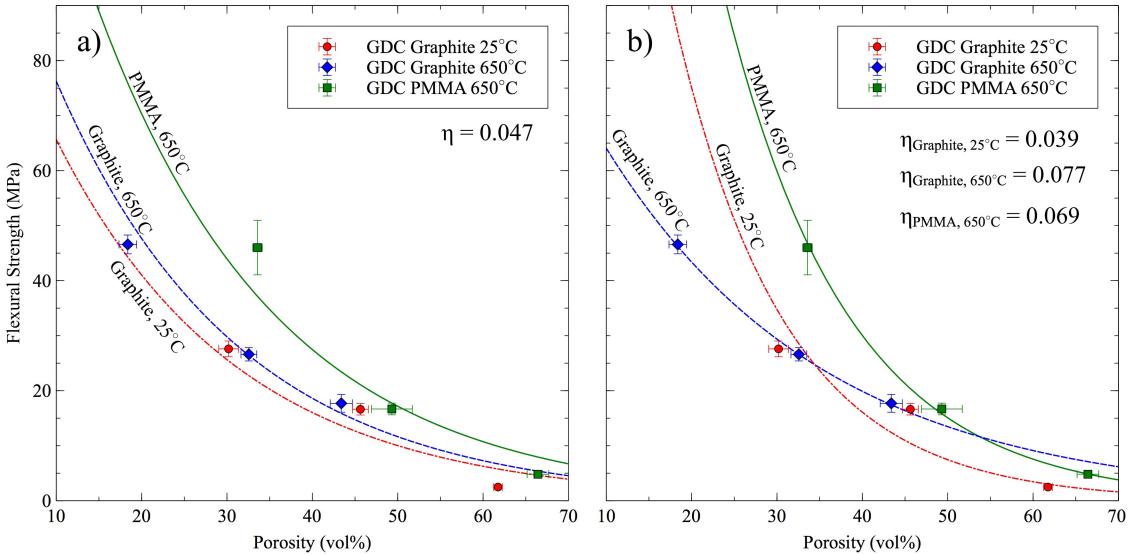


Figure 3.1: Flexural strength-porosity dependence for porous GDC10 at 650 °C and 25 °C using spherical PMMA or graphite flake pore former: a) Measured strengths fitted using fixed geometric constant; b) Measured strengths fitted using different geometric constants

The data was fit using this equation and both a fixed geometric constant, η , of 0.047 (Figure 3.1a) and a variable geometric constant (Figure 3.1b). Chi-squared values, indicating the divergence of the fit from the measured data for each sample set, were calculated for the two fitting methods and are displayed in Table 3.1.

The deviance from the fit curve for the fixed η method is quite large relative to the variable η fit for both sample sets tested at 650 °C. Both fitting methods are fairly poor in the case of the room temperature graphite set. The poor fitting results in this case is due to the >60% porosity samples. The flatter pore geometry caused by the graphite likely leads to comparatively greater strength loss at high porosity due to likely greater pore connectivity. The comparison between the high

Table 3.1: Chi-squared values for fixed η and variable η fits of porous GDC strength data (Figure 3.1)

Sample Set	χ^2	χ^2
	(Fixed η)	(Variable η)
GDC PMMA 650 °C	3.406	0.062
GDC Graphite 650 °C	0.668	0.008
GDC Graphite 25 °C	3.575	5.063

temperature data sets is the most useful, given this, and the fact that SOFCs operate at this temperature. The poor fit of fixed η models suggests that a material-specific η value may be an oversimplification of the porosity-stress relationship in ceramics.

Samples tested at higher temperatures displayed a slightly higher flexural strength. Generally, it is expected that increasing temperature lowers strength of dense ceramics once plastic deformation processes become activated at high temperatures. [56] Below the temperature at which plastic deformation starts to occur, temperature has a minimal effect on flexural strength of dense ceramics. For dense GDC it has been demonstrated that the strength decreases by 19% between room temperature and 800 °C. [13] Porosity changes this behavior, by essentially creating a composite material, keeping the rate of change constant or increasing with temperature. [57] For porous GDC, thermal expansion places a compressive stress on any surface flaws that are sites for crack initiation and propagation. Additionally, the porosity helps reduce bulk stresses caused by thermal expansion. These two

effects increase the material's fracture strength more than any decrease from plastic deformation at 625 °C.

Cross-sectional SEM of the fracture surfaces of the porous GDC samples, both PMMA and graphite, is shown in Figure 3.2. Figure 3.2a shows individual spherical pores left by the PMMA while Figure 3.2b has an inter-connected network of long pores left by the graphite flakes.

The differences in quality of fit between Figure 3.1a and Figure 3.1b shows that the geometric factor is microstructurally dependent. Samples with porosity formed using PMMA spheres showed significantly greater strength as compared to samples with graphite-formed porosity. This can be explained by the effect of pore geometry on crack initiation and propagation in the ceramic. If a crack enters a pore, the pore can now be considered the new crack tip. The energy required to advance the crack is highly dependent on the geometry of the tip. For a spherical pore, this geometric factor is maximized and results in higher resilience to fracture. This is summarized by Equation 3.2 where σ_o is the stress at the crack tip, c is the length of the crack tip and ρ is the radius of curvature of the crack tip. [58]

$$\sigma_f = \frac{\sigma_o}{2} \sqrt{\frac{\rho}{c}} \quad (3.2)$$

Based on the mechanical behavior of these samples, porous ceramics should be designed and constructed such that the pore geometry is as low aspect ratio as possible to maximize strength.

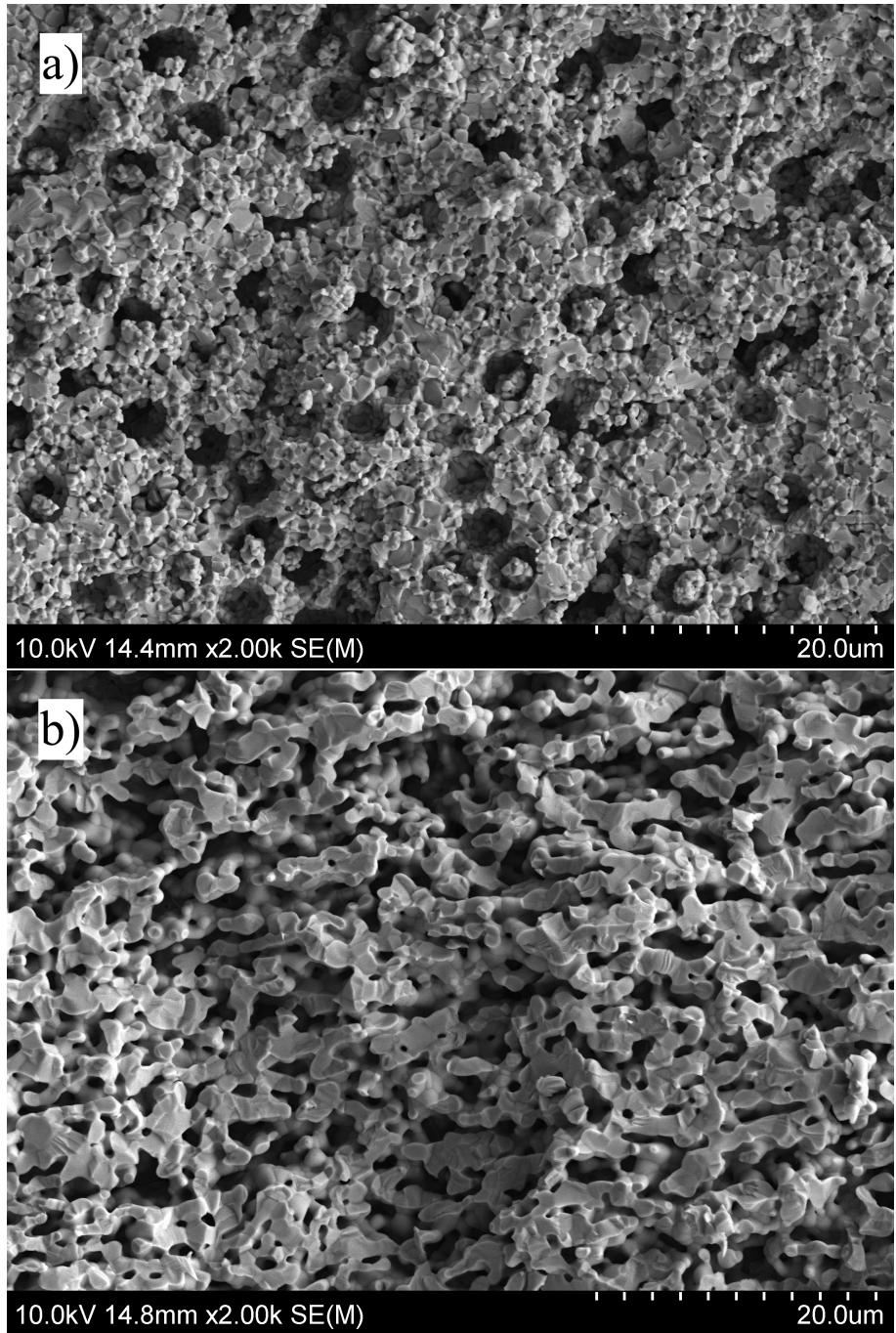


Figure 3.2: SEM micrographs of porous GDC bars made using: a) PMMA pore former; b) graphite flake pore former

3.2.2 Flexural Stress Orientation

Figure 3.3 shows the measure flexural strengths of a number of SOFC coupon samples. Anode support coupons were tested along with half-cells consisting of anode supports and electrolyte layers at temperatures ranging from 25 °C to 650 °C. The highest temperature test was repeated with coupons under reducing conditions (3% H₂, balance Ar).

All unreduced sample types showed increased strength at elevated temperatures with little difference between types at a given temperature. The high-temperature reduced coupons displayed large differences in strength depending on the orientation of the sample. Tests in which the dense electrolyte layer was placed in compression resulted in the highest strength values, while the samples were weakest when the electrolyte was placed in tension. In reduced samples, the anode support layer becomes a ceramic-metal composite and is therefore somewhat elastic while the electrolyte remains a brittle ceramic. The electrolyte-in-compression condition maximizes the mechanical performance of the coupon by placing the layers in their preferred stress state.

Figure 3.4 shows the box plots for the unreduced SOFC coupon samples. A Student's t-test was used to statically determine if the means of samples tested at different conditions were equal based on 95% confidence. There is no discernible difference in the strength between the three sample types at each temperature. At elevated temperature there was a significant difference in the modulus of ASL only samples and samples with electrolyte in tension with a p-value of 0.0091. This

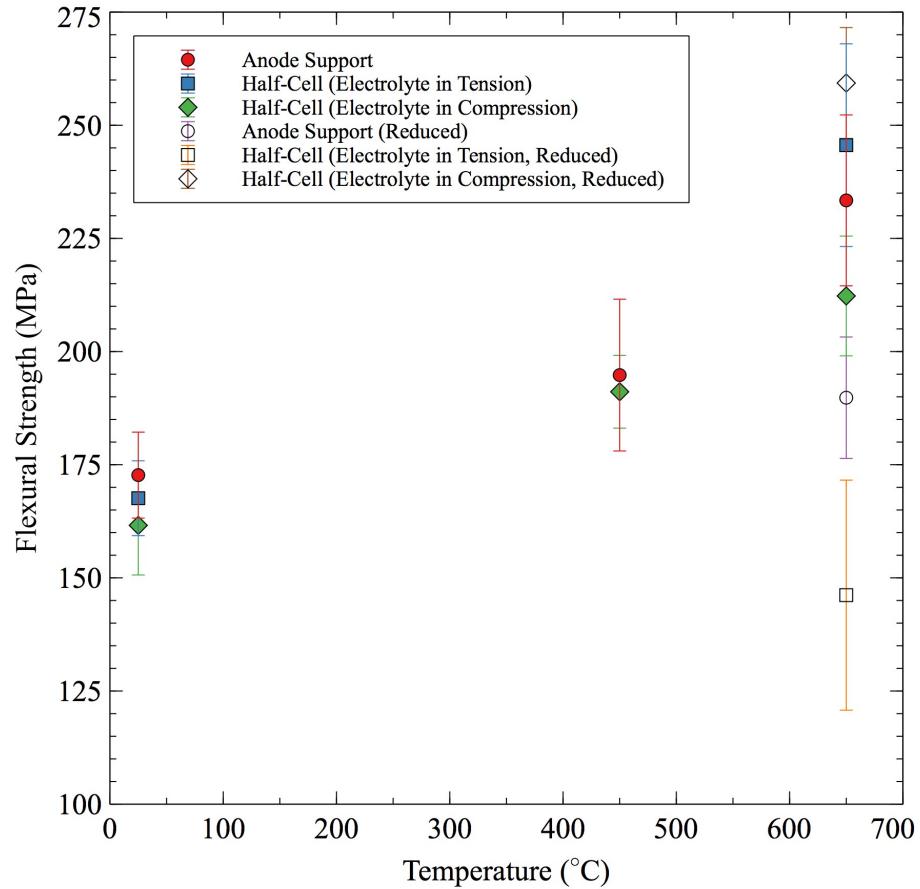


Figure 3.3: Temperature dependent strength of Ni-GDC anode supports and half-cells in both air (filled data points), and reducing atmosphere (3% H₂, balance Ar, hollow data points), tested in both “electrolyte-up” and “electrolyte-down” orientations resulting in the electrolyte layer experiencing tension and compression, respectively

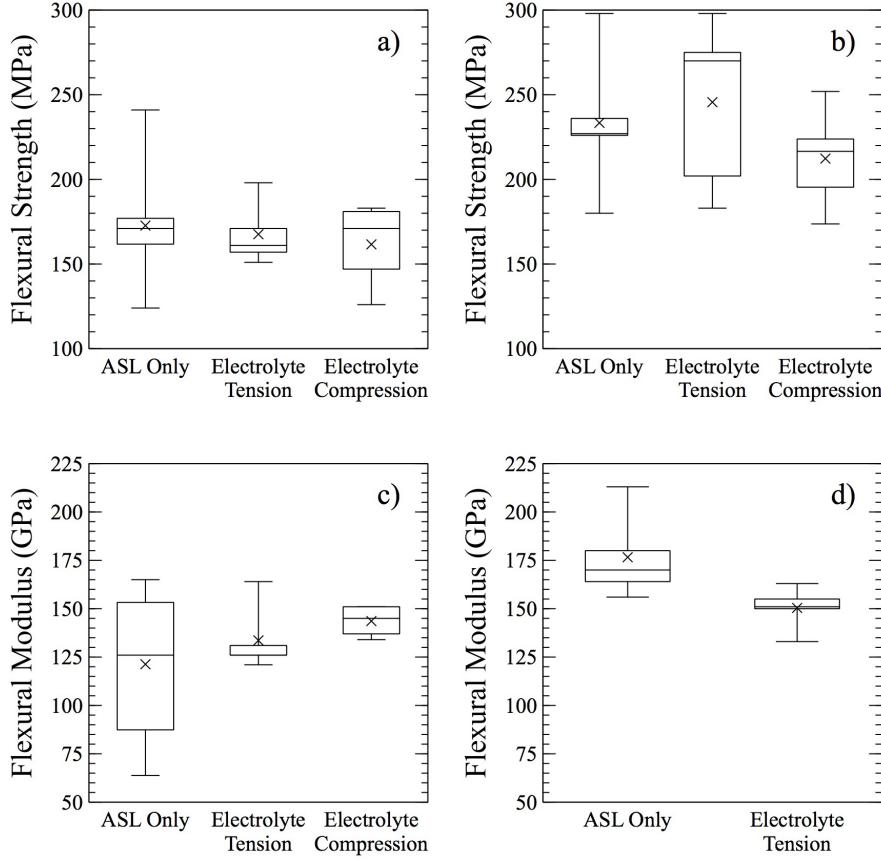


Figure 3.4: Flexural test measurements of coupons sample sets: a) Strength at 25 °C b) Strength at 650 °C c) Modulus at 25 °C d) Modulus at 650 °C

difference was not present at room temperature. As the materials reach elevated temperature, small differences in elasticity become magnified due to different thermal effects on dense and porous layers.

Additionally, SEM analysis of the fractured half-cells showed very good adhesion between layers (Figure 3.5). Delamination is a common failure mode in layered ceramics and one that would be particularly damaging to SOFCs due to resulting ionic conductivity loss between layers. [59] In the half-cell coupons, it was clear that

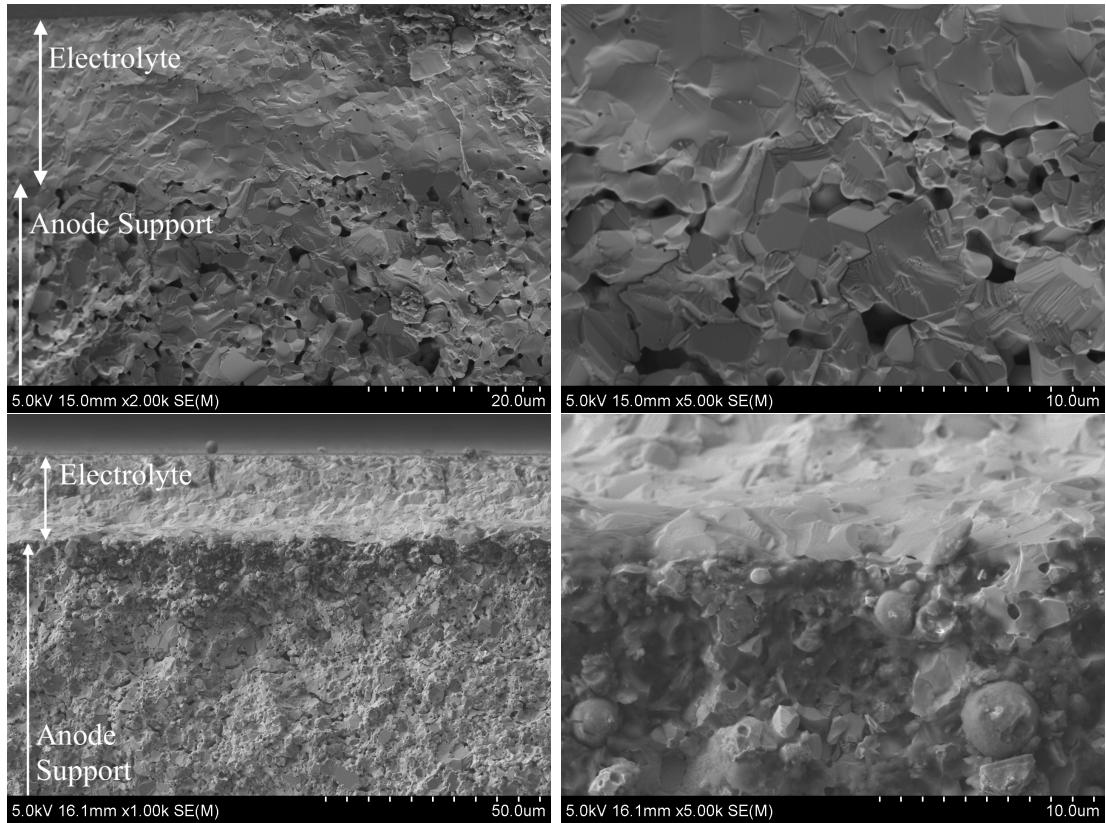


Figure 3.5: SEM micrographs of unreduced and reduced half-cell fracture

surface: tested in air at 25 °C (top) and tested in reducing atmosphere at 650 °C (bottom), showing good adhesion between anode and electrolyte

the fracture plane contained mixed transgranular and intergranular fracture. Some grains were sheared through while others remained whole. The striations visible in Figure 3.5 are characteristic of fracture proceeding through a grain, while other grains remained whole.

3.2.3 Reduction and Strength

Mass loss of SOFC half-cell coupons exposed to reducing atmosphere at various elevated temperatures is shown in Figure 3.6. Mass loss is attributed to the reduction

Table 3.2: Summary of fit parameters for reduction of NiO-GDC/GDC half-cell coupons under 3% H₂, 3% H₂O, 94% N₂ at different temperatures.

Temperature (°C)	Exponential Rate (h ⁻¹)	Asymptote (Mass %)
550	0.0463	89.78
575	0.135	89.09
600	0.182	88.36
650	0.512	87.75
750	0.821	87.87

of NiO, used as a precursor in fabrication, to Ni metal, which serves as the catalyst for fuel oxidation and electronic conductor, and the reduction of ceria to CeO_{2-δ}. Ni-GDC/GDC half cells showed the expected trend of increasing reduction rate at higher temperatures. Reduction curves were fit to an exponential decay and the summary of parameters is shown in Table 3.2. At 650 °C and 700 °C the reduction occurs very quickly, reaching steady state values after 18 hours. 550 °C showed a much slower mass loss than even 575 °C. At temperatures lower than 550 °C the kinetics are slow enough to tolerate a brief exposure to oxygen without re-oxidizing the sample. Of note in the reduction is that each temperature appears to approach a different asymptote, showing that the amount of NiO and GDC reduced at steady state is dependent on the temperature of the cell. This will affect the mechanical properties of the cells as it changes both the porosity and amount of nickel metal in the samples.

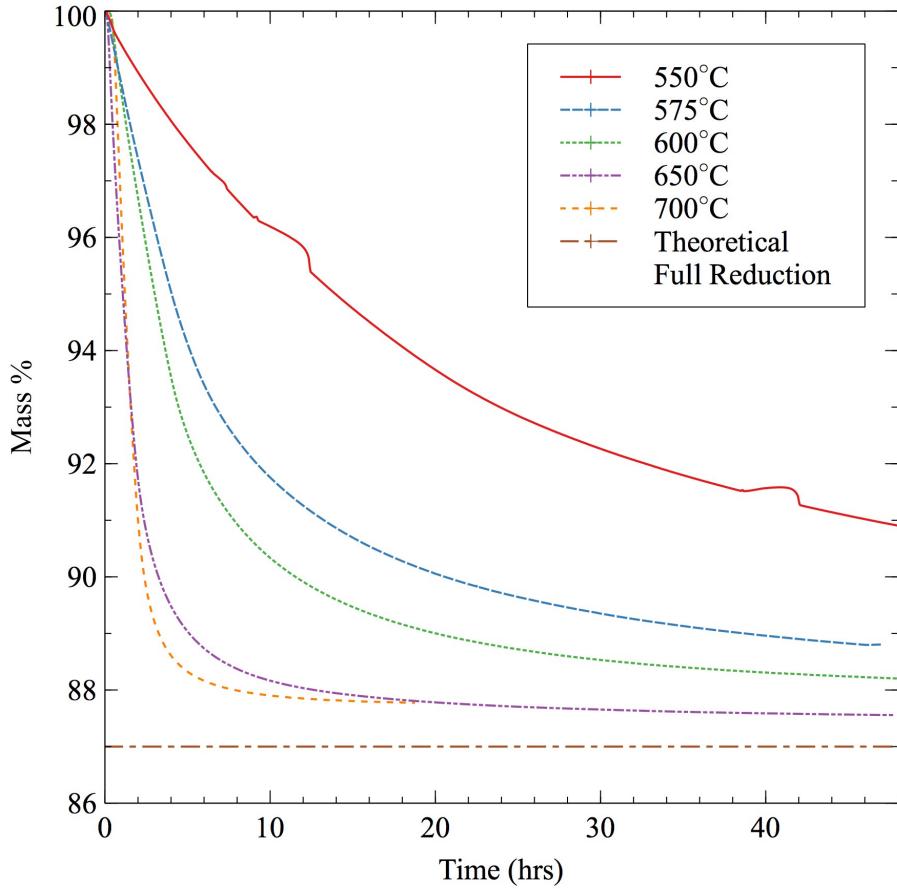


Figure 3.6: Thermogravimetric analysis curves for Ni-GDC/GDC half-cells showing mass loss over time at temperatures ranging from 550 °C to 750 °C in 3% H₂ 3% H₂O balance N₂, 50 sccm flow.

Ni-GDC/GDC fuel cells are sensitive to re-oxidation once reduced. Re-oxidation causes fracture of cells due to the large volume difference between NiO and Ni. [45] Based on the results from the TGA, the reaction rates below 300 °C are sufficiently slow to allow for the exposure of a reduced cell to oxygen without detrimental results. [60] To confirm this a sample was measured by TGA to ensure no mass gain during oxygen exposure and the strength of samples were tested to ensure there was no discernible difference between reduction methods.

For TGA analysis, a piece of a half cell was heated to 650 °C with a $10\text{ }^{\circ}\text{C min}^{-1}$ ramp rate and reduced. It was then cooled while still under reducing atmospheres. Once below 100 °C, it was exposed to simulated air (21% O₂) for 18 hours, placed back into reducing atmosphere, and heated back up to 650 °C. Figure 3.7 shows the change in mass overlaid onto the temperature and oxygen partial pressure experienced by the sample. Following this treatment, the cell showed no mass gain during the oxygen exposure and continued to reduce at the same rate as before once it was returned to the initial conditions. This shows that cells which are cooled appropriately do not re-oxidize and could be handled in between a batch reduction of cells, and their assembly into a stack configuration.

Box plots of flexural strength and modulus of the in-situ reduced and batch reduced coupons are shown in Figure 3.8. Mechanical strength of half-cell coupons which had been reduced in-situ with an 18 hour reduction time showed no difference in strength when compared with coupons which had been previously batch reduced, cooled, and reheated under reducing environments. Both of these sample types showed a dramatic decrease in strength and Young's modulus compared to the un-

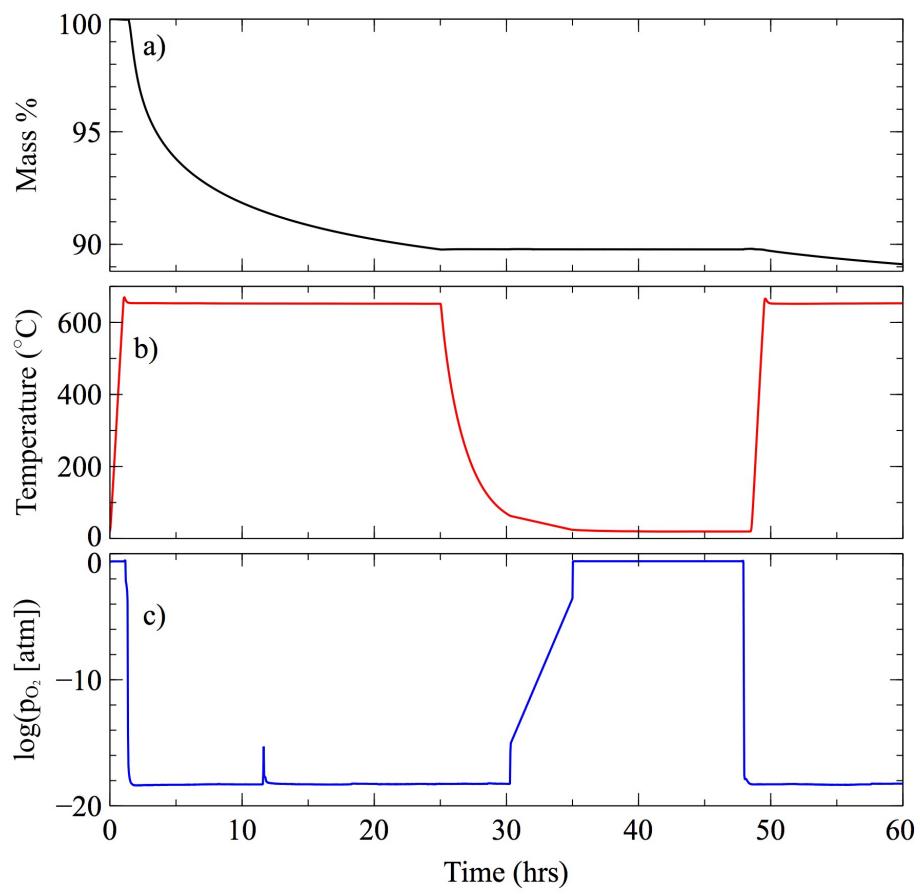


Figure 3.7: Thermogravimetric analysis of Ni-GDC/GDC half-cell showing no mass gain after reduction and exposure to room temperature and simulated air: a) Mass loss of interrupted reduction with exposure to ambient condition; b) Temperature of sample during cycle c) Oxygen partial pressure measured at the sample during cycle

reduced samples, but no statistically significant difference between treatments. The decrease in strength and modulus is due to the increase in porosity and conversion of NiO to metallic nickel in the cells. The decrease in variation between measurements in reduced cells is likely due to the increased number of large voids that form during NiO reduction.

The statistical similarity of the properties of the samples reduced via each method indicates that planar, Ni-GDC/GDC based SOFC ASL and half-cells are able to be safely reduced, cooled, and handled in ambient conditions without leading to damaging re-oxidation of the nickel anode material. This resilience could enable some degree of large-batch reduction of cell anodes prior to SOFC stack assembly, leading to more rapid startup and a greater degree of sealing control.

3.3 Conclusions

A temperature and atmosphere controlled three-point bend fixture was designed and built for use in a universal testing machine. SOFC coupons and component materials were evaluated for flexural strength at room temperature and IT-SOFC operating temperatures. In addition, the effects of porosity percent and pore geometry on flexural strength in GDC were investigated. Furthermore, the impact of temperature on the reduction rate of NiO in NiO-GDC SOFC anodes was examined along with the resilience to re-oxidation at ambient conditions of this SOFC component.

Pore geometry had a significant impact on the flexural strength of GDC10, with spherical pores showing the greatest resistance to fracture. This supports the

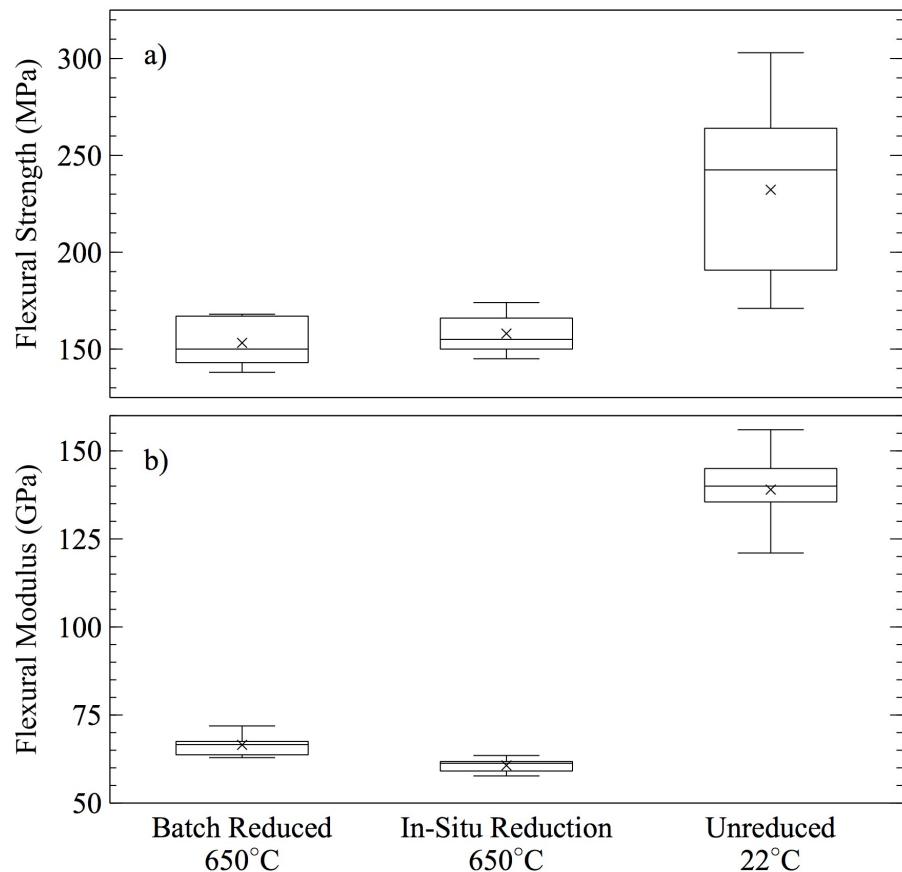


Figure 3.8: Flexural properties, a) strength and b) modulus, of Ni-GDC/GDC half-cell coupons after reduction via two different methods, compared to unreduced cells. Strength and modulus show decrease upon reduction but no significant difference between methods.

concept of pores acting as the new crack tip once a crack has advanced to the pore. Additionally, samples tested at 650 °C were stronger than those at room temperature. This is likely due to localized compressive stresses from thermal expansion of the material. This hypothesis is further supported by the results of testing NiO-GDC anode support coupons and half-cells. Coupons tested at 25 °C, 450 °C, and 650 °C displayed a linear strength dependence with temperature. There was no statistical difference in strength between anode support layers and half-cells composed of anode support and electrolyte at a given temperature in air. Half-cells in which NiO was reduced to Ni by exposure to H₂ at 650 °C displayed significant differences in strength when the electrolyte layer was subjected to compressive stress as opposed to tensile stress. Placing the ceramic electrolyte in compression and the metal-ceramic composite anode in tension resulted in the highest strength.

The reduction temperature of NiO-GDC/GDC half-cells was shown to have an effect on the rate of NiO reduction and amount of NiO reduced. At lower temperatures, the oxidation rate of Ni-GDC is slow enough that the anode can be exposed to air for significant periods below 100 °C. Any re-oxidation, combined with the cooling and re-heating of a cell back to 650 °C, showed no effect on the mechanical properties when compared to cells which had been reduced in-situ at 650 °C. These results indicate that it is possible to reduce and cool cell components to an extent without any additional effects to mechanical properties, allowing for more flexibility during cell manufacturing, stack assembly, and with quality control screenings.

This work leads to three important conclusions for the mechanical properties of

GDC-based SOFCs using Ni anodes. Porous GDC used in anode supported SOFCs should be fabricated such that the pore geometry is spherical as this maximizes energy required to advance a crack through the ceramic. Care should be taken in stack construction to ensure any out-of-plane cells are placed to compress the electrolyte and place the reduced anode in tension so as to lower the chance of fracture. Finally, it is possible to reduce the anodes of Ni-GDC SOFCs and then handle them at ambient conditions for quality control and stack assembly. This will remove a degree of variability from the manufacture of cells and stacks.

Appendix A: Statistics

A.1 Student's t-test

A.2 Weibull Statistics

Appendix B: TGA Manual

B.1 Theory of Operation

Thermogravimetry works on the principle of measuring small changes in mass as the environment changes. Changes in environment can come from changing temperature or gas composition. This system uses a Cahn microbalance to measure mass, a furnace to heat the sample up to 1100 °C and mass flow controllers (MFCs) to control the gaseous environment.

B.2 Mass Measurement

The TGA uses a Cahn D200 microbalance for the mass sensing capability. The microbalance works by measuring the current required to maintain balance between the sample and a counter balance. The sample can be hung at two different points on the arm of the balance, Loop A or Loop B. The choice of loops determines the capacity and sensitivity of the measurements, as shown in Table B.1. Full specifications are given in the microbalance manual. Loop A is used most commonly for its increased sensitivity.

The microbalance has an independent flow of nitrogen gas to it to maintain

Table B.1: Cahn D200 Microbalance Specifications

	Loop A	Loop B
Capacity (g)	1.5	3.5
Maximum Weight Change (mg)	150	750
Sensitivity (ug)	0.1	1
Repeatability	10% total load on both pans	

an consistent atmosphere. Only a small amount of flow is required (5 to 10 sccm) to keep positive pressure, but if the protective cover is removed additional time will be required to purge the balance.

B.2.1 Setup and Operation

Alignment of the balance is key to producing a low noise signal. Ideally, the hang-down wire should run through the center of the tubes and at minimum it must not touch anywhere or allow the sample pan to touch the walls of the furnace. The hang-down wire is made from platinum or a platinum-rhodium mixture and is in two pieces, to facilitate the changing out of the bottom portion incase of contamination and degradation. To successful methods of straightening the wire are to lay it flat on a surface and roll it out from the center, similar to working dough, or to hang it with a weight and soften it using heat allowing it to stretch straight. Hooks on the ends are created using tweezers and a razor blade for a sharp bend.

With the hang-down wire straight and in place, the furnace tube can be adjusted

to place the sample pan in the middle, equidistance from all walls. Moving the tube can be achieved by adjusting the supporting clamp at the bottom of the furnace or adjusting the insulation holding it in place at the top. Alignment usually requires looking straight down the tube from above the microbalance. A light can be placed at the bottom of the tube, replacing the thermocouple, to give illumination as to the location of the sample pan in the tube. Alternatively, the furnace can be heated to 800 °C so that the tube and pan glow, giving a better light, but adjustments must wait for the furnace to cool. Usually, both methods are used, the flashlight for a first alignment and the hot furnace to check afterwards.

With everything aligned, the counterbalance needs to be properly adjusted. Place on the sample pan any appropriate crucible which will be used and open the microbalance cover and remove the cover from the counterbalance by gently pulling. At this point, the microbalance is turned off using the switch on the back of the microbalance controller unit. Counterbalance weights are added or removed to have the empty sample pan and crucible balance with the counter. A light touch to the arm of the balance may be needed to off-set static and friction, but ensure this is done with clean tweezers. Once the system balances, or does so as closely as possible, the covers may be replaced and the balance turned back on. Static, especially in the winter time, commonly causes the counterbalance to swing wildly as the cover is placed back over it. Using an un-gloved hand or wiping the inside down with deionized water help reduce the static.

The thermocouple in the bottom of the furnace should be placed as close to the sample as possible. To achieve this, the thermocouple is incrementally raised

while observing the mass readout from the microbalance. Once the balance becomes unstable or jumps, the thermocouple should be backed out 0.5 to 1 cm and tightened in place. Covering the thermocouple is a quartz sheath to act as a thermowell and protect the thermocouple. If changing between materials systems or significant degradation has occurred to the thermowell it should be replaced.

At this point the system should be burned out to remove any contamination on the sample pan or hang-down wire and time is needed for it to stabilize. The furnace should be heated to 1000 °C for 4 hours in an oxygenated environment. This also provides time for the system to stabilize, as monitored by creating a run with the MicroScan Acquisition software. It can take up to 24 hours for it to stabilize. If random jumps occur in the mass, recheck the alignment and thermocouple placement.

After stabilization, a sample can be loaded in to a crucible and sample pan. While the microbalance is calibrated to measure the mass of the sample added, it is good practice to measure and record the mass using a separate balance beforehand. Crucibles may be reused where appropriate. After the sample is placed the furnace is raised, slowly to ensure not altering the alignment, and connected to the fittings above. The furnace should be at the maximum height position when finished. Time should then be given to allow the mass reading to stabilize before starting a test.

The program MicroScan Acquisition controls the TGA and records data. After opening, select “Balance > Establish Connection” to connect to the D200. If an error occurs, power cycle the balance, restart the program, and check the serial cable leading to the balance. Upon successful connection, the current read out of the balance will be displayed. The balance maybe tared before adding a sample,

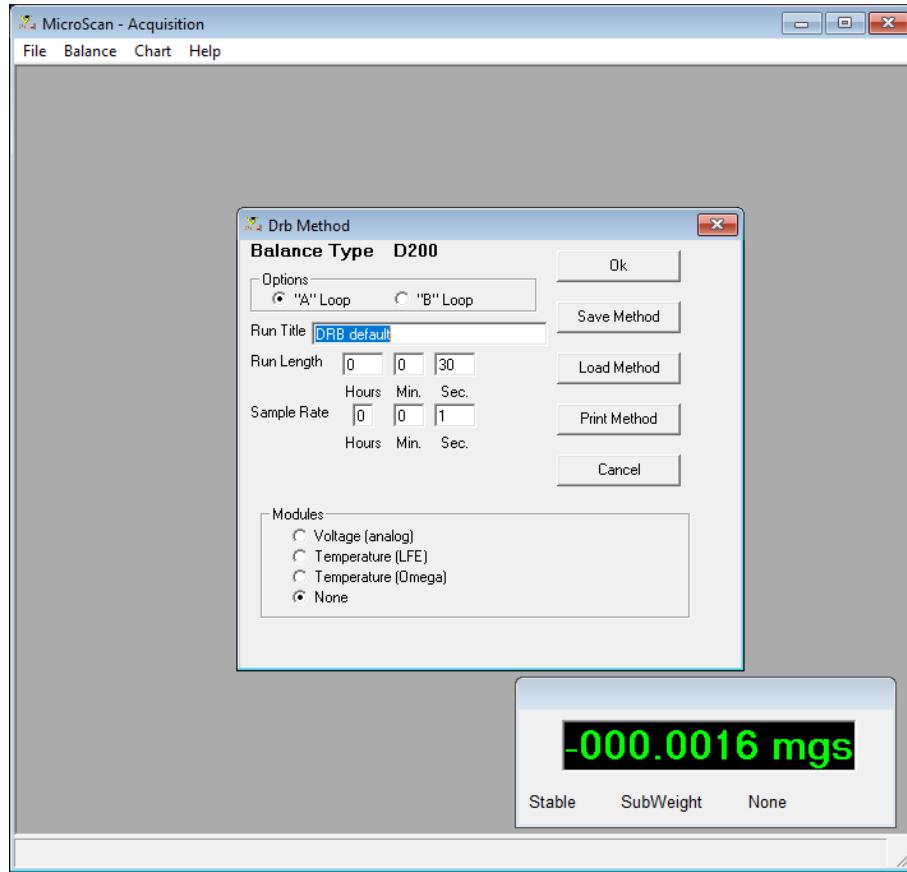


Figure B.1: MicroScan Acquisition with Open Method open and the current read out of the balance displayed

by selection “Balance > Tare.” Starting a new run is achieved by selecting “File > Open Method.” Figure B.1 shows the “Open Method” screen with the current balance read out from MicroScan Acquisition.

From here the total length of the run is defined along with the sample rate. The sample rate will need to match the rate given in the other programs. Additionally, the run title can be defined and the loop can be changed if needed. Once the run length and sample rate are entered, selecting “Ok” brings up the menu where the run can be started. By clicking “Start Run” the MicroScan Acquisition asks for the

location to save the data in a proprietary format, and once the file path is given, it then starts collecting data. During the run, collected data is plotted and can be viewed using the controls at the top of the plot. After a run is complete, the saved file is converted to a csv by opening it with MicroScan Analysis and selecting “File > Export... > Comma/Tab Separated...”

B.3 Heating

Heating is done by a furnace surrounding the YSZ tube and sample. It is controlled by a Eurotherm controller and reading are taken from a thermocouple placed inside the YSZ tube. As a result, there is a lag in the system between the furnace elements heating and the thermocouple sensing the heat. The controller can be programmed with up to 8 segments in the temperature profile and programming can be performed from the front panel of the unit or by the Eurotherm iTools software. The iTools software must be closed before attempting to use the LabVIEW program which reads the temperature from the controller.

B.4 Gas Delivery

Gas flows are controlled by the MKS Type 647C Multi-channel Flow Ratio/-Pressure Controller and the individual MKS Type M100B MFCs. Each MFCs controls one gas by measuring the flow with a thermal mass sensor and adjusting it using a valve to meet the desired set point. Each MFC has a rated size and must have the zero and gas correction factor (GFC) properly set. The zero can be set

physically using a screw on the MFC if a large adjustment is needed or electronically using the controller. The zero should be set with both sides of the MFC open to the atmosphere to ensure no leak from a left over pressure differential. The GFC can be theoretically calculated based on the heat capacity of the gas compared to a standard. This assumes that the MFC is properly calibrated, which may not be a safe assumption. As such it is best to calibrate the MFC by adjusting the GFC so that it measures correct flow rates as given by a bubble meter.

If an MFC leaks despite being set to off, the tension spring for the valve located inside the MFC may need adjustment. The manual for the MFC outlines the procedure. If the tension is correct and the valve still leaks, service is advised. An alternative is to add an external shut off valve, which can be closed either manually or automatically. This has been implemented for one of the current MFCs.

Different gases can be supplied to the MFCs as needed for the experimental setup. If the gas to an MFC is changed, a new GFC will need to be obtained. Gases can be humidified after the MFC with the use of a bubbler, but they should not be humidified beforehand for risk of damaging the MFC. Care should also be taken when mixing or changing gas compositions to avoid potentially dangerous combinations, such as mixing fuels and oxidizers. When changing between a reducing and oxidizing environment, it is good practice to allow sufficient time for a sweep gas (such as N₂) to reduce the risk of the different atmospheres mixing.

The MFCs can be controlled by a computer with LabVIEW. They can either be manually set or given a scheduled program to follow. Typically a constant total flow rate will be used among all tests. 50 sccm is a good starting point for the total

flow rate. After turning on the MKS controller, the master flow control must be turned on by pushing “ON” followed by “0/All.”

B.5 pO₂ Measurement

pO₂ of the gas flow is measured by a home-built YSZ sensor located after the MFCs combine into one flow. Gas flows down a two bore alumina tube along with a platinum wire to the end of a YSZ tube. The wire is lightly connected to the inside of the YSZ tube using platinum paste. The gas then flows in the reverse direction, between the alumina and YSZ tubes to the outlet. Outside the YSZ tube at the end, a separate piece of platinum wire is connected to the end of the tube. This setup is then placed in a furnace and heated to 800 °C where the difference of partial pressure can be measured according to the Nernst equation. Voltage potentials from the two wires are measured by a Keithley 2000 digital multimeter.

Once the system is setup, very little needs to be done to maintain the sensor. If it must be cooled for a power outage or to be worked on, a ramp rate of 1 °C min⁻¹ is to be used to avoid damaging the YSZ tube. For accurate pO₂ measurements, after any modification a calibration curve needs to be created using a reference meter. Voltage measurements and pO₂ calculations are recorded by the computer using a LabVIEW program.

B.6 Controls

Almost all of the components of the thermogravimetric analysis (TGA) system are computer controllable. As previously mentioned and explained, the microbalance is controlled by the MicroScan Acquisition program. LabVIEW programs interface with the Keithley, MKS controller, and Eurotherm temperature controller.

B.6.1 Gas Controls

Gas flows can be controlled with either the Gas Controller or Gas Scheduler programs. Gas Controller allows for the immediate control of any gas flow channel while Gas Scheduler changes the gas flows at predetermined times allowing for the automated changing of composition. Figure B.2 shows the front panel of Gas Controller, Figure B.3 is the front panel of Gas Scheduler, and the code for both programs is explained in Appendix C.2

To start using Gas Controller ensure proper channels are set for the MKS Controller Port, Arduino Port, and Servo Channel. On and Off position adjust the position of the external shutoff valve controlled by the Arduino. These values should only change if changing USB to serial adapters or with new hardware. Starting the LabVIEW program immediately begins the control to gasses to the specified values. The radio buttons on the left turn channels on or off and set them to the set point. To end the program push the STOP button. The program displays the current reading for the flow to ensure flow is occurring as specified.

The Gas Scheduler requires the input of a tab delimited text file, referred to as

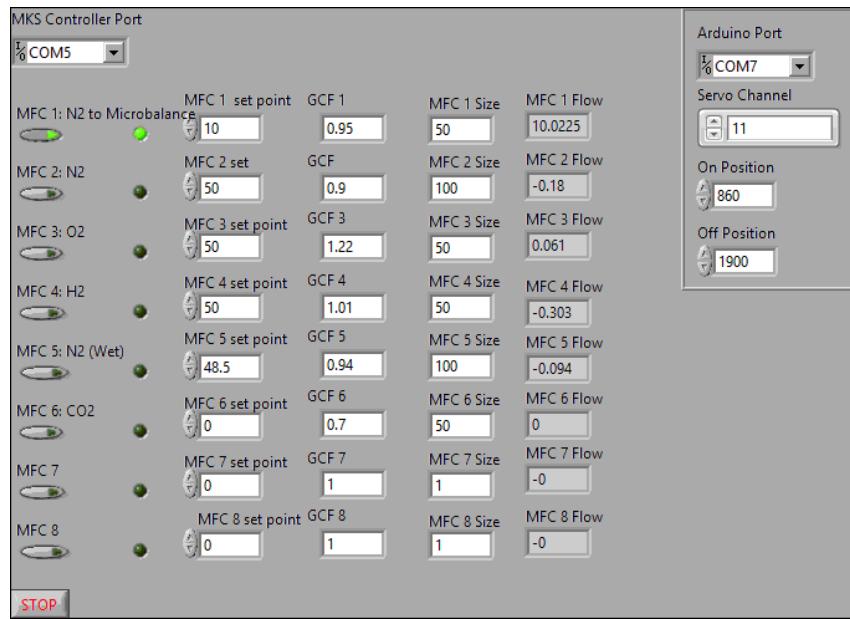


Figure B.2: Front panel display of Gas Controller program

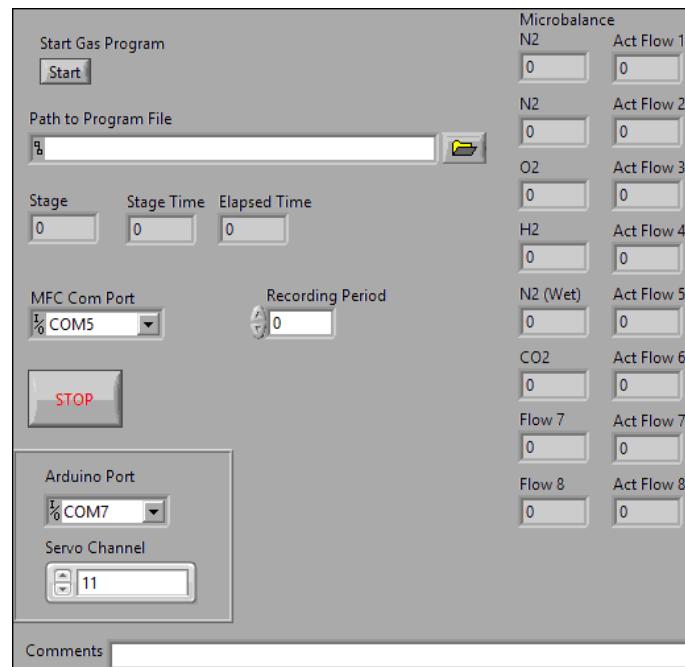


Figure B.3: Front panel display of Gas Scheduler program

a schedule. An example schedule comes with the program. In this schedule the time for the desired gas flow is given in seconds, followed by the set point of each channel. The program ends on the row with a negative time value, retaining those set points.

Before starting the program, the file path to the schedule must be given by clicking the folder icon next to the Path to Program File field. Again, ensure that the com ports and channels are correct. The program records the measured flows at a set interval, as defined by the Recording Period (in seconds) and records them to a comma separated value (csv). Additionally, comments can be added to the csv in the optional comments field. After starting the program, the start button needs to be pressed.

B.6.2 Temperature and p_{O_2} Measurements

The program Temp & pO₂ Measurements reads the values from the Eurotherm controller and the Keithley multimeter, plots them, and records the results to a csv. Figure B.4 shows the front panel of the program with the user controls.

Before running the program ensure that the com ports and channels are correct. The Measurement Period should match that given to MicroScan Acquisition. By enabling the timer, the program will stop after the designated time. Comments can be added to the csv file by filling in the File Comments field. When the program starts running, it will ask for the location to save the csv. As a note, the timer for the program starts as soon as the program does, before defining the csv location, but the first measurement does not occur until afterwards.

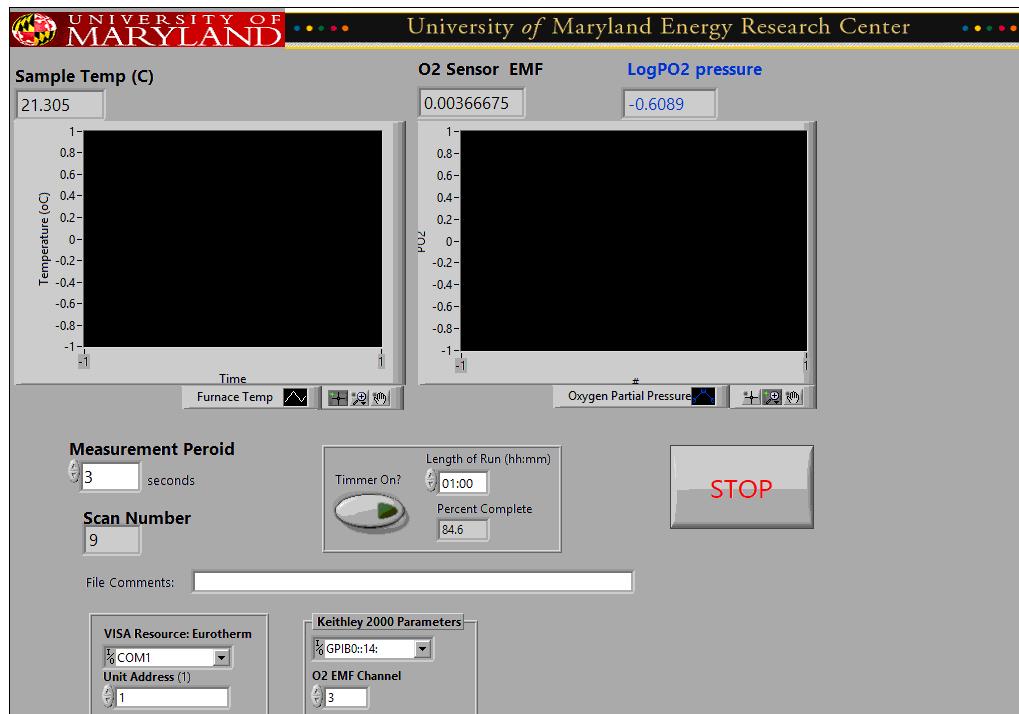


Figure B.4: Front panel display of Temp & pO₂ Measurements program

B.6.3 Starting a Run

Multiple programs need to be started simultaneously for a run of the TGA. Because each program starts differently, the following is a recommendation for the order to start the programs. on how to minimize differences in timers between the program. Time values from MicroScan should then be used in subsequent analysis. This procedure minimizes the amount of time difference between measurements on the TGA, temperature and pO₂.

To begin, enter all values in to the various programs. In MicroScan Acquisition, follow the full setup, including clicking Start Run, but stop immediately afterwards with the file browser up. In Temp & pO₂ Measurements, follow the full setup

including designating where to save the data. As soon as the file path to save data is given, switch to MicroScan Acquisition and complete the setup giving it the file path also. If using Gas Scheduler, start that program as normal followed by the temperature program on the Eurotherm.

B.7 Interfacing with other devices

The effluent of the TGA can be fed to other devices for advances analysis, such as a mass spectrometer (MS). When doing this, one thing to note is physical distance between the TGA and the other instrument. The longer the gas line connecting the two the instruments, the longer it will take gas to travel from one instrument to another. During this time period, diffusion will occur up and down the line, broadening any signal to the second instrument. This delay and broadening effect will need to be investigated for each experimental setup.

B.8 Troubleshooting

- **Unsteady mass:** check alignment and thermocouple placement
- **No gas flow on any channel:** check master flow control
- **No gas flow on one channel:** check the channel is on and manual valves are open
- **MFC leaks when off:** Check zero, adjust spring tension as described in MFC manual, add external shutoff valve or return for repairs

- **No or noisy voltage from pO_2 sensor:** Check wire connections from sensor,
rebuild sensor with new platinum paste

Appendix C: Code

The programs referenced in this appendix are published as open-source software and are in the public domain. The code and latest versions of all parts are available on GitHub at <https://github.com/patrickstanley/> with the provided repository names and contributions are welcome.

C.1 Arduino PID Relay Furnace Controller with Serial Connectivity

The purpose of this Arduino sketch is to power a heating furnace (controlled by a solid-state relay) with PID controls. In addition, serial communications are used to monitor, log, and interact with the controller. A running average is used to reduce thermocouple measurement noise for the derivate component of the controls.

This sketch is available at <https://github.com/patrickstanley/arduino-pid>.

C.1.1 Hardware and other libraries

This was built to be used on a Arduino Uno R3, but should be easily run on a variety of different boards. For temperature sensing, an [Adafruit MAX31856](#) is used with the provided [library](#). Also used is the PID controller [library by br3ttb](#). This sketch pieces the two libraries together and adds serial communications functionality.

C.1.2 Variables

The following is a list of control variables which may be changed per setup.

- RelayPin: The physical pin the relay is connected to.
- Adafruit_MAX31856(CS, DI, DO, CLK): Pins for the MAX31856
- WindowSize: Length of on/off cycle, needed to account for AC power
- printdelay: Delay time in milliseconds for printout on serial
- MaxOP: Maximum operating power, used to extend life of elements
- myPID(&Input, &Output, &workingSet,P,I,D, DIRECT): PID values need to be adjusted for the particular setup. If inverse behavior is experienced (e.g. heats when it should cool) switch DIRECT.
- workingSet and Setpoint: Initial setpoint for power on
- ramrate: Sets a ramp rate for the working setpoint. Measured in milliseconds for 1C change.

C.1.3 Serial communications

Baud rate is set to 9600. Output is tab delimitated of Setpoint, Working Setpoint, Thermocouple Temperature, and Output Power. To change Setpoint, send a new number over serial and press return. The endline character of the serial monitor may have to be changed send \n as end of line.

C.1.4 Arduino Sketch

```
1 #include <Adafruit_MAX31856.h> //loads library for thermocouple reader
2 #include <PID_v1.h> //loads PID library
3 #include <RunningAverage.h> //loads class for Running Average
   ↳ calculations
4 #define RelayPin 2 //set pin number which is connected to power relay
   ↳ for device
5
6 const byte numChars = 32;
7 char receivedChars [numChars]; // an array to store the received data
8
9 boolean newData = false; //trigger to determine if data needs to be
   ↳ read
10
11 Adafruit_MAX31856 max = Adafruit_MAX31856(4, 5, 6, 7); // Software SPI,
   ↳ Pin number for: CS, DI, DO, CLK
12
13 //Define Variables
14 double workingSet, Setpoint, Input, Output;
15 int WindowSize = 1000; //Length of cycle for power on/off
16 unsigned long prevprintMillis = 0;
17 const long printdelay = 5000; //delay amount before printing via serial
18 unsigned long windowStartTime;
19 unsigned long prevRampTimer = 0;
20 unsigned long MaxOP = .95; // Max Operating Power
21
```

```

22 RunningAverage myRA(10); //Set up running average with # of
    ↪ measurements
23
24 PID myPID(&Input , &Output , &workingSet ,250 ,50 ,8 , DIRECT); //Specify the
    ↪ links and initial tuning parameters
25
26 void setup() {
27     pinMode(RelayPin , OUTPUT); //define RelayPin as an output
28
29     //staring serial communications
30     Serial.begin(9600);
31     Serial.println("PID Controller Output");
32     Serial.println("Setpoint\t Working SP\t TC Temp\t Output"); //tab
        ↪ delimited for logging
33
34     //setup for thermocouple reader
35     max.begin();
36     max.setThermocoupleType(MAX31856_TCTYPE_K); //change type if needed
37
38     windowStartTime = millis(); //start timer for duty cycle window
39
40     myRA.clear(); // explicitly start clean
41
42     //initialize the variables we're linked to
43     workingSet = 20;
44     Setpoint = 20;
45

```

```

46 myPID.SetOutputLimits(0, MaxOP * WindowSize); // tell the PID to range
        ↪ between 0 and the full window size
47 myPID.SetMode(AUTOMATIC); // turn the PID on
48 }
49
50 // function to receive data via serial and process when endmarker is
        ↪ received
51 void recvWithEndMarker() {
52     static byte ndx = 0;
53     char endMarker = '\n'; // define line endmarker for client
54     char rc;
55
56     while (Serial.available() > 0 && newData == false) {
57         rc = Serial.read();
58         if (rc != endMarker) {
59             receivedChars[ndx] = rc;
60             ndx++;
61             if (ndx >= numChars) {
62                 ndx = numChars - 1;
63             }
64         }
65     else {
66         receivedChars[ndx] = '\0'; // terminate the string
67         ndx = 0;
68         newData = true;
69     }
70 }
```

```

71 }
72
73 //Function to repeat new setpoint for confirmation
74 void showNewData() {
75   if (newData == true) {
76     String recievedString = String(receivedChars);
77     Serial.print("Setpoint changed to ... ");
78     Serial.println(recievedString.toFloat());
79     Setpoint = recievedString.toFloat();
80     newData = false;
81   }
82 }
83
84 void loop() {
85   recvWithEndMarker(); //check for new setpoint
86   showNewData(); //sets new setpoint and displays it
87   myRA.addValue(max.readThermocoupleTemperature()); //add themocouple
88   ↪ read to rolling average
89   Input = myRA.getAverage(); //sets PID input to rolling average value
90   myPID.Compute(); //calculate PID output
91
92 //print delay for serial output so not to flood logs
93   unsigned long printMillis = millis();
94   if (printMillis - prevprintMillis >= printdelay) {
95     prevprintMillis = printMillis;
96     Serial.print(Setpoint); Serial.print("\t"); Serial.print(workingSet);
97     ↪ Serial.print("\t"); Serial.print(max.readThermocoupleTemperature()

```

```

    ↵ () ; Serial.print("\t") ; Serial.println(Output/WindowSize*100);

96 }

97

98 //turn the output pin on/off based on pid output

99 if ( millis() - windowStartTime >= WindowSize)

100 { //time to shift the Relay Window

101     windowStartTime += WindowSize;

102 }

103 if (Output < millis() - windowStartTime) digitalWrite(RelayPin,LOW); //  

    ↵ HIGH and LOW set to default off

104 else digitalWrite(RelayPin,HIGH);

105

106 //sets ramp rate functionality

107 unsigned long ramptimer = millis();

108 unsigned long ramprate = 6000; //milliseconds for 1C change

109 if (workingSet != Setpoint)

110 {

111     if (ramptimer - prevRampTimer >= ramprate && workingSet < Setpoint)

112     {

113         workingSet++;

114         prevRampTimer = ramptimer;

115     }

116     if (ramptimer - prevRampTimer >= ramprate && workingSet > Setpoint)

117     {

118         workingSet--;

119         prevRampTimer = ramptimer;

120     }

```

```
121     }  
122 }
```

C.2 MKS Gas Controller and Scheduler

The purpose of these LabVIEW programs is communicate and control MFCs for remote and automated operation of the TGA. Individual MFCs can be turned on or off and have their set point changed. After basic controls are developed a new VI, a scheduling program is provided which reads a text file automatically changing flow rates are predetermined times. The VI gas controller and gas scheduler VIs, along with a sample gas schedule, are available under the GitHub repository “mks-mfc” The VIs are saved for LabVIEW version 2013 and later. This work is the continuation and development of programs previously written by others.

C.2.1 Hardware and other libraries

These programs are written for the use of a MKS 647C Multi Channel Flow Ratio/Pressure Controller with Type M100B MFCs. It can accommodate up to 8 channels for MFCs and communicates via serial. Drivers for LabVIEW communications with the MKS 647C are available online from the National Instruments (NI) website. Serial communications occur over the VISA standard and require the installation of the VISA drivers from NI.

An Arduino Uno R3 is utilized with a servo motor and 3D printed parts to manually turn a shut off valve, compensating for a leaking MFC. Details on the installation of the Arduino controlled shut-off including STL files for 3D printing

are available at <https://hackaday.io/project/52519-automated-gas-flow-shut-off>. To control the Arduino from LabVIEW the LINX library is used and must be downloaded from the VI package manager. Additionally, the Arduino will need to be flashed with the LINX control sketch before use. This component can be easily removed if not required for the application.

C.2.2 Program Overview

The block diagram of the Gas Controller VI which manually controls the MFCs is provided in Figure C.1 and is the fundamental starting block for the gas scheduling program. Starting on the far left of the program, initial communications variables such as baud rate and port information are passed to the sub-VIs which open communications. The program then enters a while loop until the stop button is pressed or an error occurs, at which point serial communications are closed by the appropriate sub-VI.

Within the while loop, the program sequentially goes to each channel, checking the desired status, setting the control variables and reading the flow. If the program is set to not use an MFC, the internal valve is shut and the flow is read to ensure no leakage. If an MFC is set to be used, the percent of full flow is calculated based on the size of the MFC, the gas correction factor, and the desired flow rate. The percent of full flow is then passed to the MFC and the flow is read. For the case of channel 3, which posses a leaky MFC, the addition of an external shutoff valve controlled by Arduino was implemented. If channel 3 is to be used, the Arduino

sends a pulse width modulation (PWM) signal to the servo motor which corresponds to the valve being in the open position. In the case where channel 3 is to be closed, a PWM signal is sent which closes the valve.

Finally, after each channel has been set, the program checks for the dangerous combination of hydrogen and oxygen gasses. If the channels for hydrogen and oxygen (in this case channels 3 and 4) are both open, the program immediately shuts the valves and gives an error warning the user and ends the program. As long as this is not the case, the program proceeds to loop back to setting the values for channel 1.

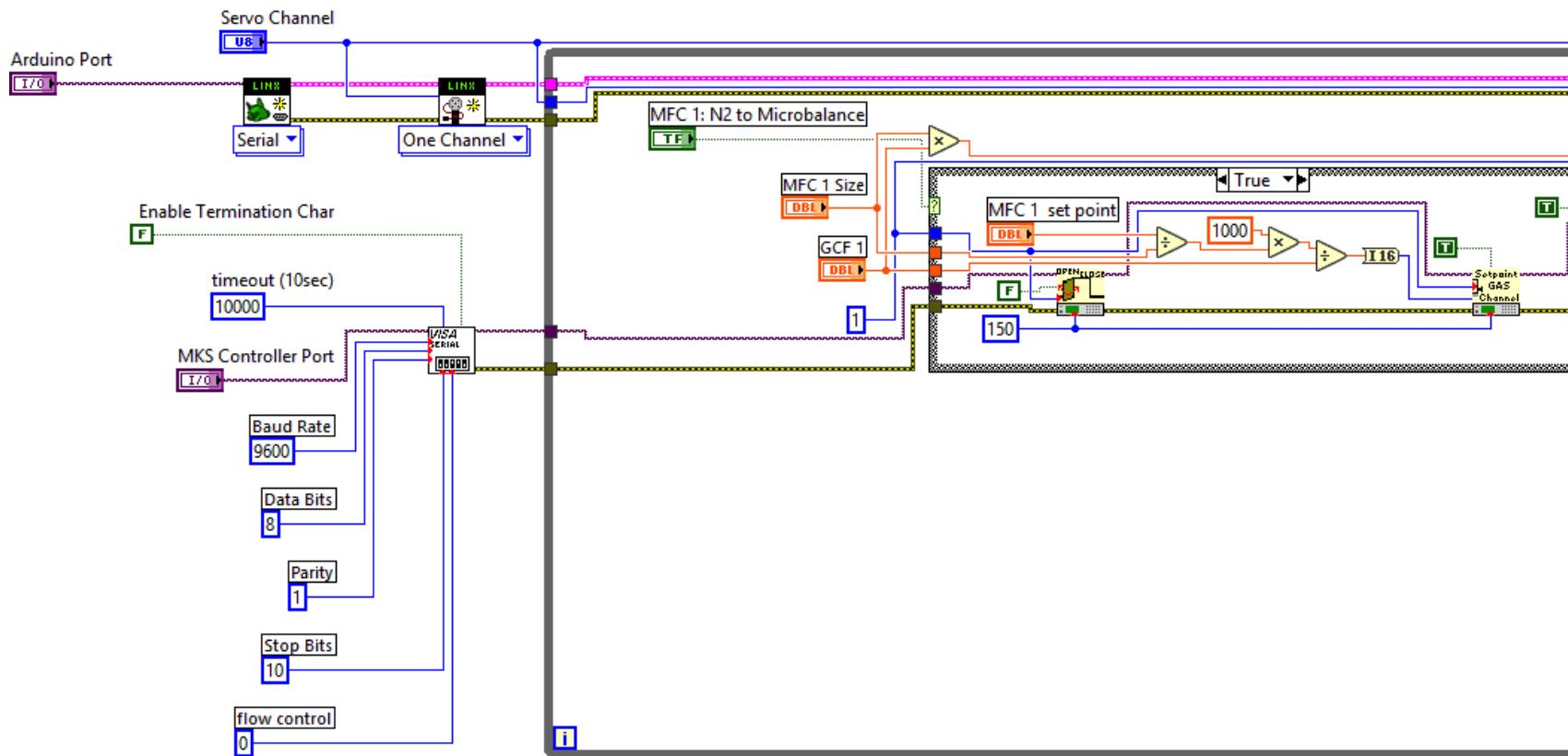


Figure C.1: MFC Controller program

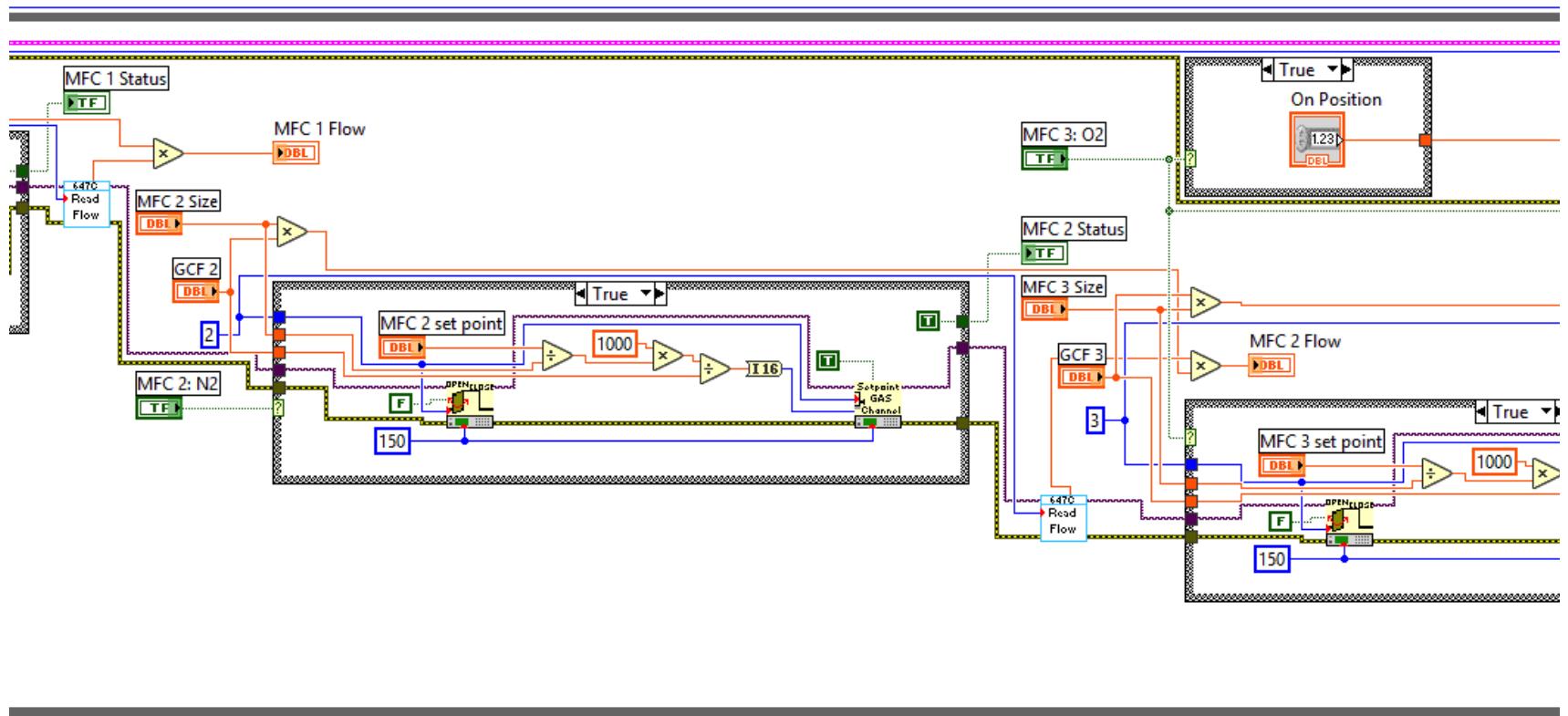


Figure C.1: MFC Controller program (cont.)

G5

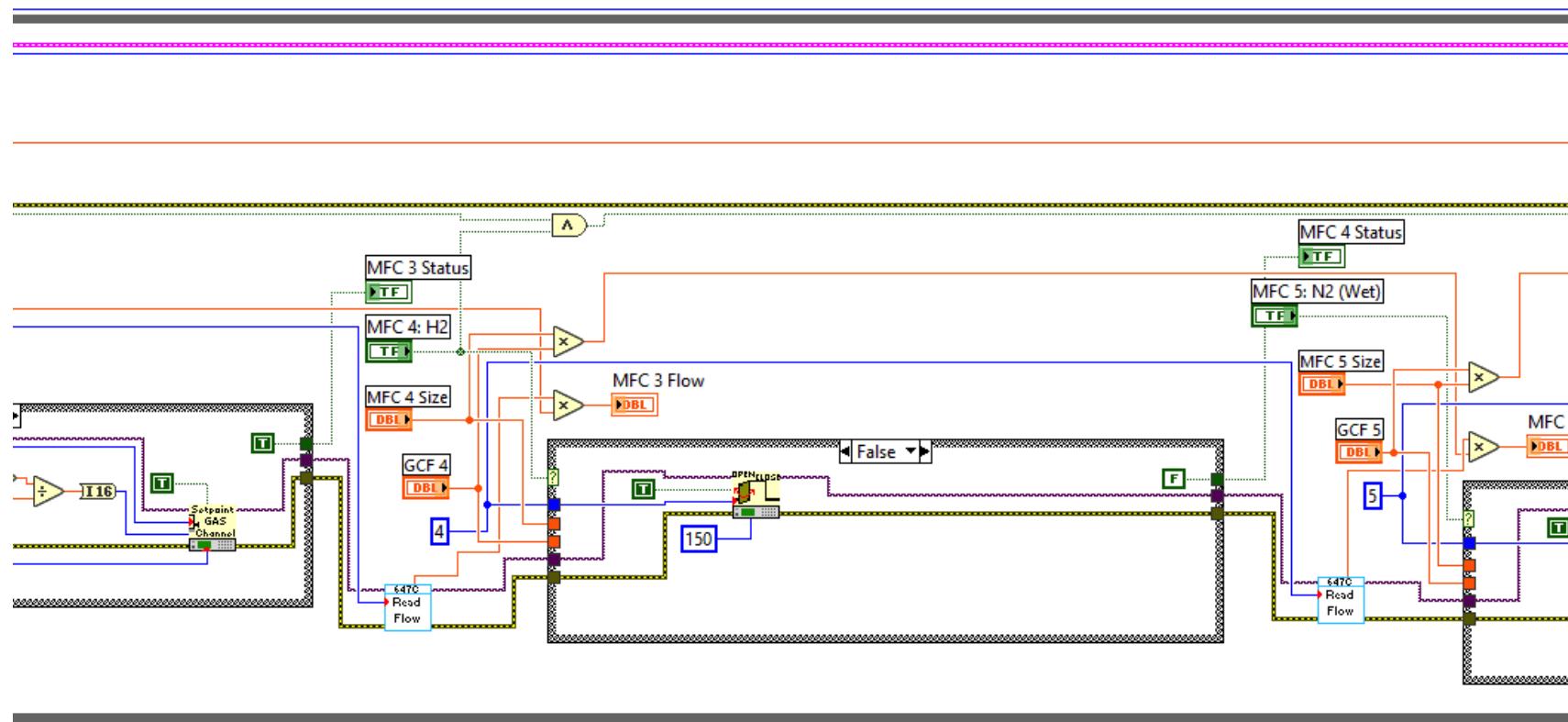


Figure C.1: MFC Controller program (cont.)

16

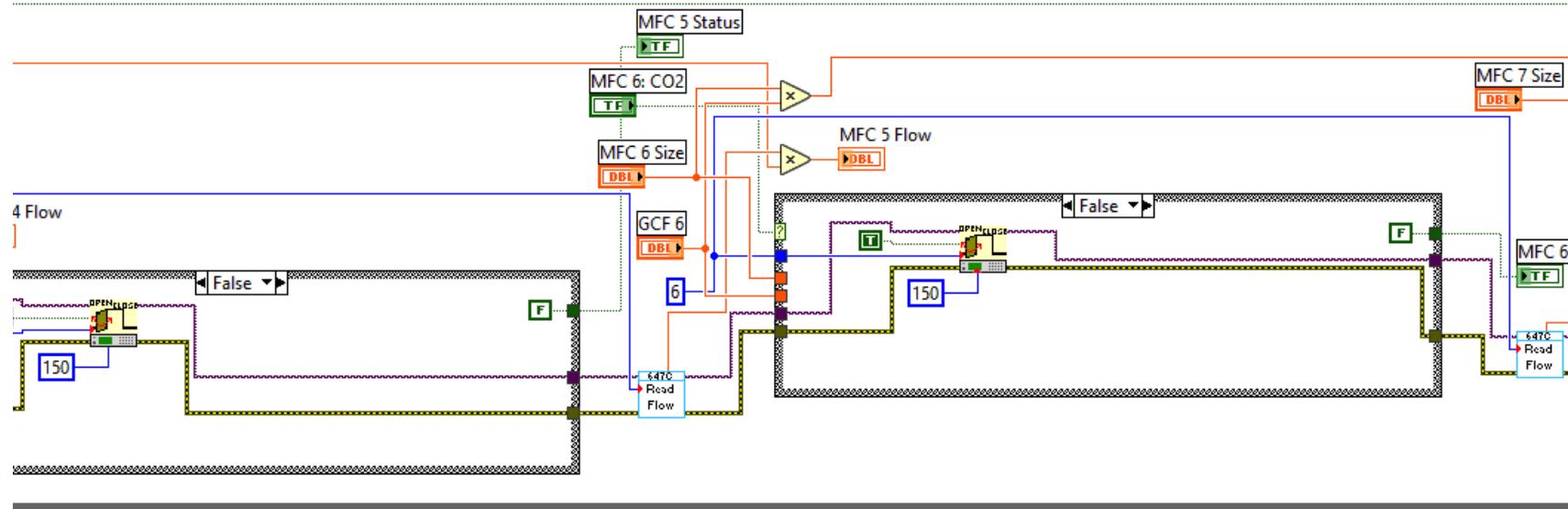


Figure C.1: MFC Controller program (cont.)

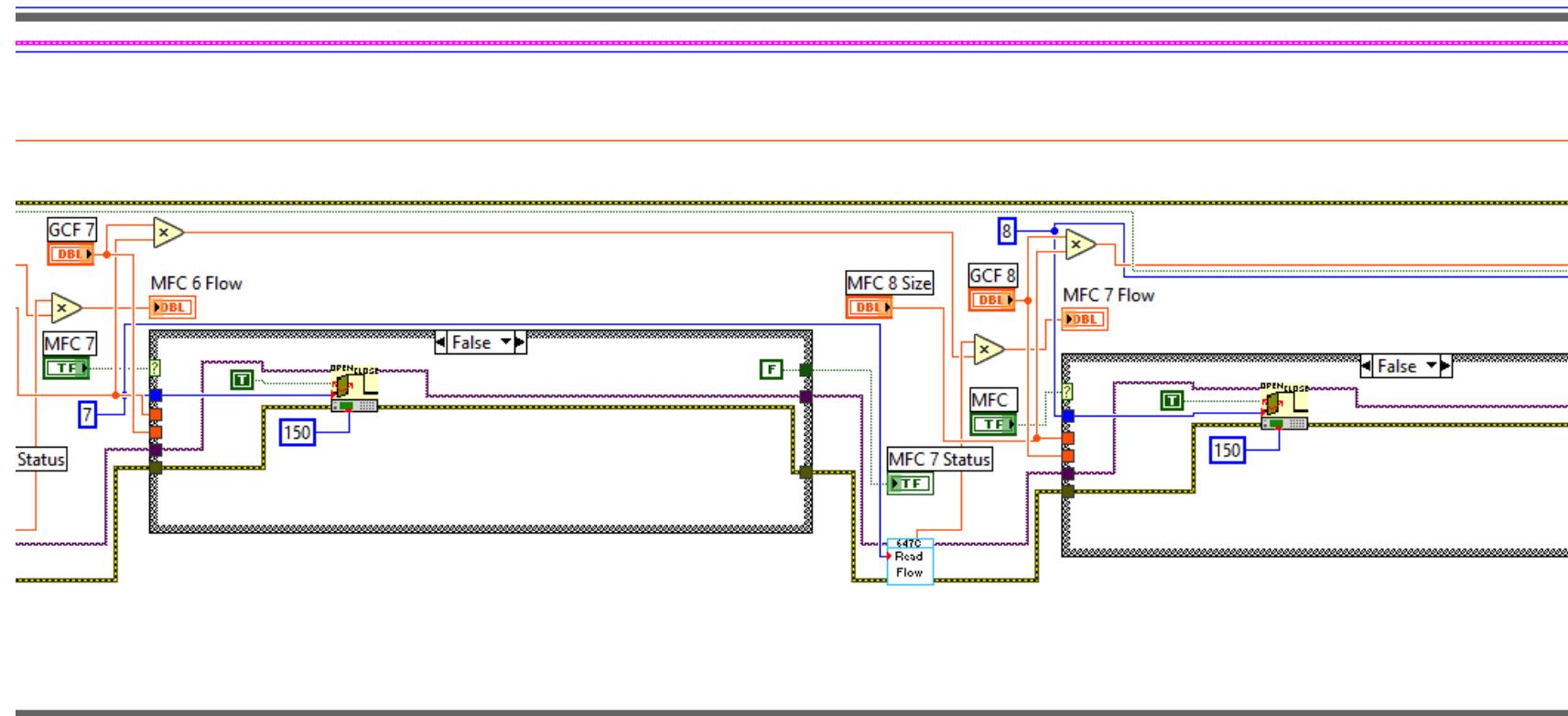


Figure C.1: MFC Controller program (cont.)

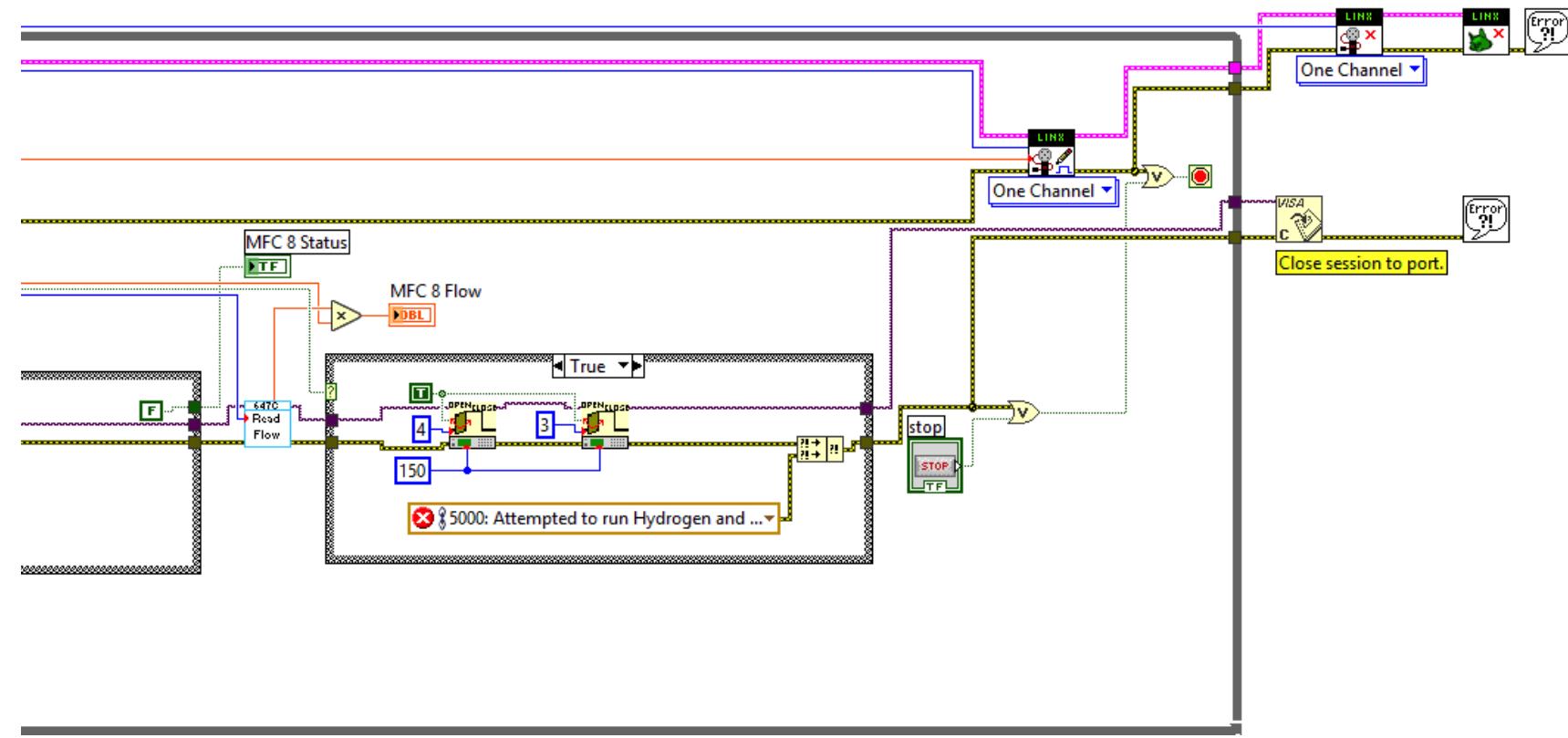


Figure C.1: MFC Controller program (cont.)

The Gas Scheduler program uses the Gas Controller to automate the switching of gasses based on the instructions provided in a text file. The text file, referred to as the gas schedule, is a nine column tab delimited file where the first column is the amount in seconds for which that gas flow is to be run, followed by the flows for each channel. The program sequentially goes through the rows until it encounters a negative time, at which point it ends leaving that row's gas flows running. The program also additionally records the measured flows to a csv file for manual inspection later.

Figure C.2 gives the block diagram of the program. Before the start of the program the path to the gas schedule must be specified. At the start of the program, the location to record measured gas flows is requested and setup as a csv file type with a header, variables to count the row of the program and time elapsed are initialized and communications variables are passed to sub-VIs. After this, the program enters a while loop. This while loop is ended if an error occurs, if the stop button is pressed, or if the amount of time in the stage (given by the first column in the gas schedule) is less than zero.

Once the start button is pushed, a timer is started to measure the amount of time elapsed in the stage. If the time has elapsed the amount prescribed (starting with zero seconds), the program reads the gas schedule, increments the stage number, and passes the flow rates to a gas controller sub-VI, after which the VI loops. If time has not elapsed, the program records the flows based on a second elapsed time timer to limit the total number of recordings. After a program end condition is met, the communications channels are closed.

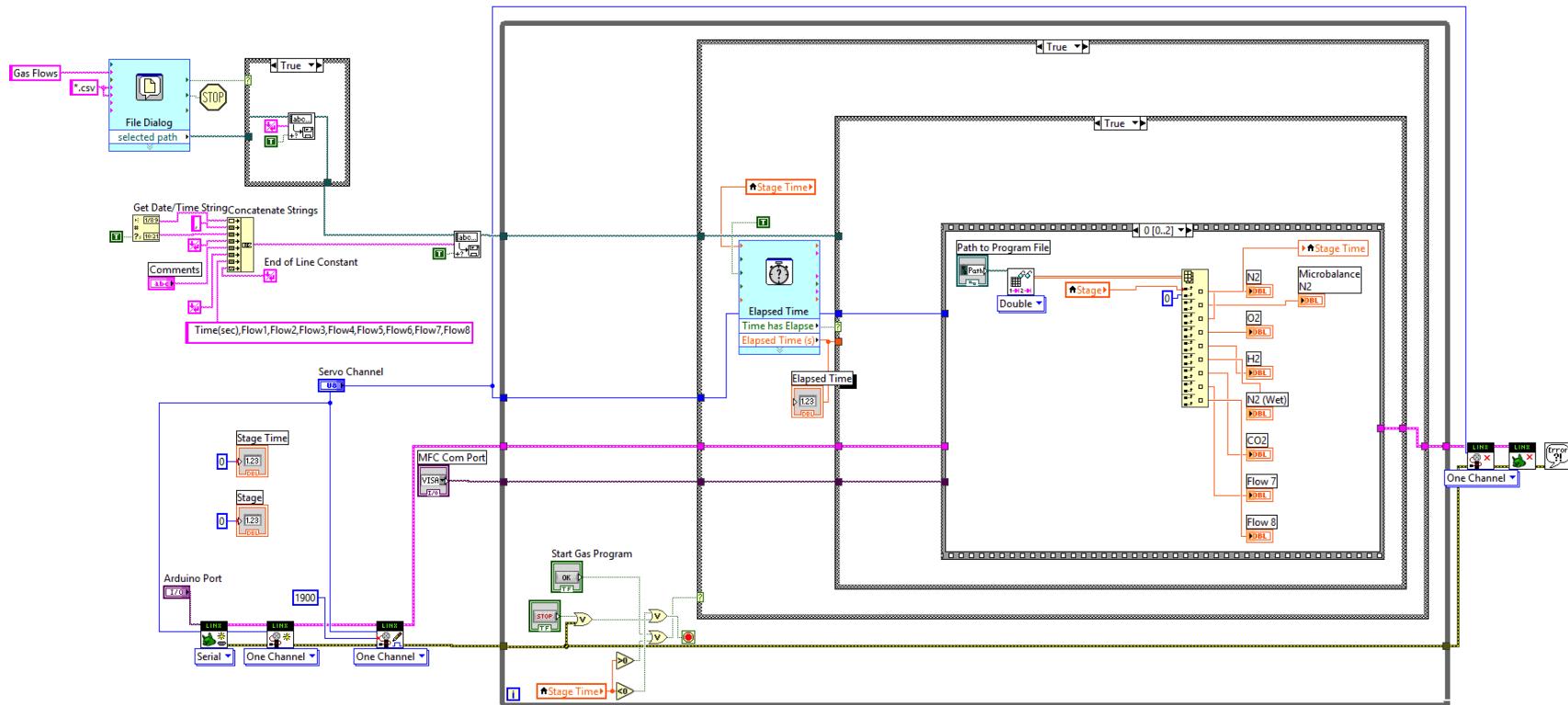


Figure C.2: Gas Scheduler program

C.3 Temperature and p_{O_2} Measurements

The purpose of this LabVIEW program is to periodically measure the temperature from a Eurotherm process controller and calculate p_{O_2} based on voltage from a Keithley multimeter for the TGA system. The VI is available on GitHub under the repository “eurotherm-keithley-measure” and is saved for LabVIEW 2013 and later. This work is the continuation and development of programs previously written by others.

C.3.1 Hardware and other libraries

Temperature measurements are taken directly from a Eurotherm 2408 controller with optional serial communications module. A driver package for all 2400 series Eurotherm controllers is available form the NI website. Serial communications again occur by VISA and require the NI VISA drivers.

p_{O_2} was calculated from voltage measurements taken of a YSZ sensor by a Keithley 2000 digital multimeter. Communications were established with the Keithley via GPIB (IEEE-488) and thus require the NI-488 driver from NI. Additionally, drivers for the Keithley 2000 are available online from NI and are required for the VI.

C.3.2 Program Overview

A copy of the block diagram is given in Figure C.3. When started, the program asks for the location to save the measurements. The program then creates the csv

file time in seconds, the voltage read, the calculated log p_{O_2} , and the temperature from the controller. Communications variables, such as baud rate and channels, are sent the appropriate sub-VIs to begin communications to the device and a timer is started. The program backs up the Keithley's current settings, resets the device and prepares it to measure voltage on one channel, while displaying "Running" on the front panel display. After the program is complete, the Keithley is reset once again and its original setting are restored before communications are closed to it and the Eurotherm.

The rest of the program occurs in a while loop. The loop is delayed a fixed amount of time, set by the Measurement Period. If the timer functionality is turned on, the loop repeats for a fixed amount of time based on the Length of Run variable, after which a stop signal is sent. During each loop, the process value (temperature) of the Eurotherm is measured and any alarms or flags are checked for. If any occur, they are passed to the error handler and the program stops. The voltage of the specified channel of the Keithley is measured and the $\log(p_{O_2})$ is calculated from it. These values are then displayed, plotted, saved to the csv file.

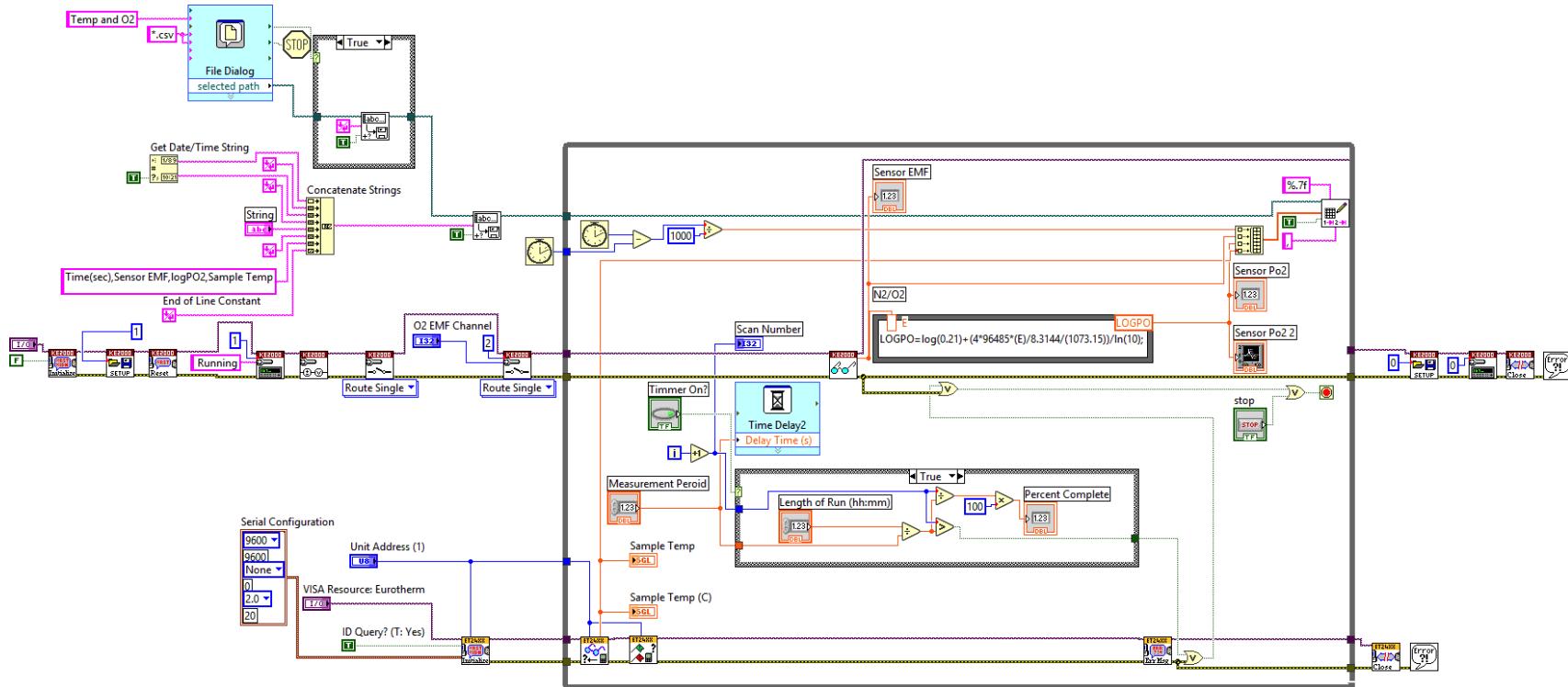


Figure C.3: Temperature and p_{O_2} measurement program

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